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AIR POLLUTION: CONTROL TECHNIQUES FOR CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

NATO Committee on the Challenges of Modern Society

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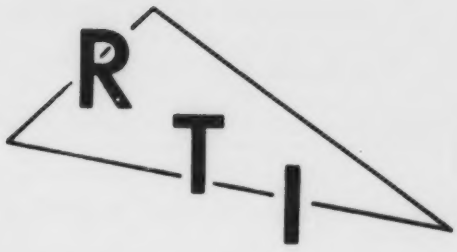

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FOREWORD

This document is a compilation of information on methods for the control of carbon monoxide emissions that was assembled by the Expert Panel for Air Pollution Control Technology, The Committee on the Challenges of Modern Society, NATO, for distribution to the member countries.

The Chairman of the Expert Panel wishes to acknowledge the efforts of scientists from the pilot countries, scientists from observer countries, and the many other persons who assisted in the preparation of this document and the four companion volumes: Control Techniques for Particulate Air Pollutants, Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources, Control Techniques for Sulfur Oxide Air Pollutants, and Control Techniques for Nitrogen Oxide Emissions from Stationary Sources.

Thanks are due the Environmental Protection Agency of the United States for permission to use their document, Control Techniques for Carbon Monoxide Emissions from Stationary Sources, which was published in 1970, as a basis for this effort. Representatives from this agency deserve special recognition.

Major contributions were made by a team of scientists from the Federal Republic of Germany under the direction of Dr. Dieter Hartmann. These contributions were invaluable to the success of the effort.

Recognition should also be given to the team from the Research Triangle Institute, Research Triangle Park, North Carolina, USA, for their efforts in literature searches, writing, and editorial work.

Lastly, acknowledgment should be given to those secretaries and other support personnel who have made the panel effort possible.

John K. Burchard, Ph.D.
Panel Chairman

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SUMMARY

Carbon monoxide found in ambient air originates from both stationary and mobile sources. Estimated emissions within the United States during 1970 are given in Table 3-1.

CARBON MONOXIDE SOURCES

By far the greatest source of CO emissions is the automobile. Other major emissions sources include forest fires, structural fires, and burning banks of coal refuse. Industrial sources include foundries, petroleum refineries, and kraft pulp mills. Burning of solid waste produces more CO than all the conventional stationary fuel combustion sources. The stationary sources of carbon monoxide are covered in this document.

CONTROL METHODS

Techniques for controlling emissions of carbon monoxide from stationary fuel combustion sources include source relocation, source shutdown, energy substitution, energy conservation and good operating practice. Various systems, used to control emissions from stationary process sources, include afterburners, waste-heat boilers, mechanical sealing, fume hoods, and waste-gas flares.

Table 2-2 summarizes the methods for controlling Co emissions from stationary combustion sources and Table 2-3 summarizes those for controlling stationary process sources.

EMISSION FACTORS

Emission factors may be used to estimate emissions from sources for which accurate stack test results are unavailable. Process emission factors for some selected source types are presented in Chapter 5.

I. INTRODUCTION

Carbon monoxide in the atmosphere may have many adverse effects upon health and welfare, and reduction of emissions of this pollutant may be of prime importance to any effective air pollution abatement program. This document has been prepared to summarize current information of carbon monoxide emissions--sources and methods of control.

Carbon monoxide originates from a variety of sources; the many agricultural, commercial, domestic, industrial, and municipal sources are described individually in this document. The nature and quantities of the emissions from the various processes are discussed, and methods of control that have been successfully applied are listed.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. The devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are the techniques generally applicable to the broad range of carbon monoxide emission control problems.

A tabulation of emission factors from which overall emissions for the various sources can be estimated is presented. Although the factors are normally for sources with no control, where applicable, emission factors are given for representative types of control.

When reference to "BRD" is made, the initials stand for Bundes Republik Deutschland (Federal German Republic).[2]

2. BACKGROUND INFORMATION

Carbon monoxide is one of the products produced by the incomplete combustion of carbonaceous material; it is formed, for instance, when carbonaceous material is burned in a reducing atmosphere, in which the available oxygen is not sufficient to burn the material completely to carbon dioxide. Because such conditions exist in the cylinders of the gasoline internal-combustion engine, and because of the large number of automobiles in use, CO emissions from this source conspicuously exceed those from any combination of other sources.

An estimated 135 Gkg of carbon monoxide were emitted from industrial, commercial, and domestic sources in the United States during 1970.[1] Table 2-1 shows the contribution to this total from each source category. Transportation is by far the largest individual emitter of carbon monoxide pollution.

Table 2-1. - CARBON MONOXIDE EMISSIONS BY SOURCE CATEGORY, 1970[1]

Source	Quantity (Gkg)	Percent of total
Transportation	100.7	74.7
Fuel combustion (stationary)	0.64	0.5
Industrial processes	10.3	7.7
Refuse disposal	6.5	4.8
Miscellaneous	16.6	12.3
	134.74	100.0

Table 2-2 . - SUMMARY OF METHODS FOR CONTROLLING CARBON MONOXIDE EMISSIONS FROM STATIONARY COMBUSTION SOURCES

Control Method	Remarks
Change of fuel or energy source Change to gas from oil and coal	Accepted emission factors for burning of coal, oil, and gas show decreasing CO emissions for these three fuels, in the order given. But CO emissions from boilers and furnaces are so low a fraction of total CO emissions that fuel change is not justified.
Change to nuclear power or hydroelectric generation	Use of nuclear power is expected to grow; hydroelectric generation will grow slowly. Nuclear power involves generation of some CO due to the periodic test operation of standby power-generating units employing conventional fuels.
Replace industrial, commercial, and household thermal requirements with central power	Generation of electric power is increasing. CO emissions are easier to control at a central power plant than at small installations and households. Efficiency is lower for indirect use of fuel through electricity than for direct burning. Reduction in local CO concentrations may result in increased oxides of nitrogen (NO_x) emissions at distant power plants.
Combustion Control Air Supply	A well-adjusted gas-fired boiler may emit less than 1 ppm of CO, but may emit more than 50,000 ppm if insufficient air always causes CO formation; too much air may do the same by flame quench.
Residence time	Short residence times tend to cause more CO in exit gases. Proper residence time allows the use of less excess air.
Temperature	High temperature is desirable, but dissociation of CO_2 into CO becomes noticeable at 1 810 K. Rapid cooling and low oxygen concentration tend to hinder recombination of CO_2. Flame temperatures above 1 920 K are conducive to formation of oxides of nitrogen (NO_x).

Table 2-2 (continued)

Control Method	Remarks
Mixing	Good mixing is very important for burning of CO; appliance and burner design should facilitate mixing.
Flame contact	Contact of flame with cold surfaces tends to form CO by quenching, i.e., it reduces residence time at effective oxidation temperature.
Change of waste disposal method	
Sanitary landfill	Replaces open-burning and incineration.
Various treatments for coal-waste piles	These are not deliberately burned, but ignite by spontaneous combustion or accident. See AP-52, CONTROL TECHNIQUES FOR SULFUR OXIDE AIR POLLUTANTS.

Table 2-3. - SUMMARY OF METHODS FOR CONTROLLING CARBON MONOXIDE EMISSIONS FROM STATIONARY PROCESS SOURCES

Source	Control method	Remarks
Iron and steel industry		
Blast furnace	CO generated is burned as fuel	Emissions can be produced by faulty equipment and accidents.
Grey iron cupola	Flame afterburner	Not all controlled.
Basic oxygen steel furnace	Burned inside hood and dispersed by stack	Collection for use as fuel not common in United States.
Sintering furnace	None	
Coke oven	Proper design, scheduling, operation, and maintenance	Controls are same as those to control particulates and SO_2. See AP-52, *Control Techniques for Sulfur Oxide Air Pollutants.*
Petroleum industry		
Petroleum catalytic cracking unit	Burned as fuel in CO boiler	CO produced during regeneration of catalyst. Burning as fuel usually requires supplementary fuel for stability.
Petroleum fluid coker	Burned as fuel in CO boiler	Gas produced in coker burning section of coking unit is rich in CO.
Chemical industry	Most commonly burned as waste	Moderate amounts generated in chemical industry as a whole, but this actually occurs only in specified segments of the industry. Emissions are from gas purging, leaks, abnormal operations such as startup, upsets and shutdown, or relief of overpressure.

2.1 REFERENCES

1. OAP Data File of Nationwide Emissions, 1970. National Air Data Center, Applied Technology Division, July 1972.

2. Carbon Monoxide-Origin, Measurement, and Air Quality Criteria. VDI Berichte Nr. 180. VDI-Verlag, Düsseldorf. 1972.

3. STATIONARY SOURCES OF CARBON MONOXIDE

Carbon monoxide (CO) is one of the products of incomplete combustion when carbonaceous material is burned in a reducing atmosphere--that is, when available oxygen is not sufficient to form carbon dioxide (CO_2). Because such conditions exist in the cylinders of the gasoline internal combustion engine and because of the large number of automobiles in use, CO emissions from mobile sources exceed those from stationary sources and account for about 60 percent of the total CO emissions.

Table 3-1 is a summary of estimated 1970 emissions of CO within the United States. No figures were available for metallurgical furnaces and the use of explosives, but figures for the other sources total approximately 90 Gkg. Table 3-2 summarizes BRD emissions of CO for 1970.

Although large amounts of CO are produced and handled by industry, most is reused as fuel or raw material so that actual emissions result only from leaks or abnormal operations. Large contributions still arise from the use of wood as fuel. The small values for burning natural gas should not convey the impression that complete combustion necessarily takes place when gas is burned; actually, copious quantities of CO can be formed if this fuel is burned with too little air.

3.1 STATIONARY FUEL COMBUSTION SOURCES

Stationary combustion sources include steam-electric generating plants and industrial, commercial, and domestic combustion units. These burn large quantities of coal, fuel oil, and natural gas (see Tables 3-3 and 3-4 and Fig. 3-1) and lesser amounts of coke oven gas or tar, coke, refinery gas, blast furnace gas, wood, or other waste- or byproduct-type

Table 3-1. - SUMMARY OF ESTIMATED CARBON MONOXIDE EMISSIONS IN THE UNITED STATES DURING 1970[1]

(Gkg/yr)

Source	Gkg	Percent of total
Transportation	100.5	74.6
Motor vehicles	87.6	65.0
Gasoline	86.9	64.5
Diesel	0.7	0.5
Aircraft	2.7	2.0
Railroads	0.1	0.1
Vessels	1.5	1.1
Non-highway use of motor fuels	8.6	6.4
Fuel combustion in stationary sources	0.7	0.6
Coal	0.5	0.4
Fuel oil	0.1	0.1
Natural gas	0.1	0.1
LPG and kerosene	0.0	0.0
Wood	0.0	0.0
Industrial processes	10.5	7.7
Solid waste disposal	6.5	4.8
Miscellaneous	16.6	12.3
Forest fires	3.6	2.7
Structural fires	0.2	0.1
Coal refuse	0.3	0.2
Agricultural burning	12.5	9.3
Total	134.8	100.0

Table 3-2. - SUMMARY OF ESTIMATED CARBON MONOXIDE EMISSIONS IN THE BRD DURING 1970[d]

Source	Emissions, Mkg/yr	Percent of total	Emission factor
Transportation	7 574	81	
Gasoline	7 230		350 kg/m^3[a]
Diesel	330		27 kg/m^3
Aircraft	14		20 kg/LTO
Fuel combustion in stationary sources	802	9	
Coal	760		45 g/kg[b]
Fuel oil	39		0.6-2 g/kg[c]
Natural gas	3		0.3 g/m^3
Industrial processes	900	10	
Municipal incinerators	4	--	
Total	9 280	100	

[a]For example, H. May, TUV Rheinland.

[b]12.6 Gkg domestic coal (coke and pit coal) Stat. Jahrbuch 1971.

[c]"Studie uber Haushaltsfeuerungen;" Batelle, Hartmann and Braun, NUKEM, 1972 fur das BMI.

[d]BRD (Bundes Republik Deutschland) Federal German Republic.

Table 3-3. - U.S. MINERAL ENERGY RESOURCES AND ELECTRICITY PRODUCTION AND CONSUMPTION: 1965 TO 1969[2]

[In 10^{15} Joules]

Year	Total	Coal		Crude petroleum[a]	Natural gas[b]	Electricity
		Anthracite	Bituminous and lignite			
1965	57 000	346	12 700	22 800	21 200	2 220
1966	60 500	306	13 500	24 000	20 500	2 230
1967	62 500	290	13 300	24 800	21 600	2 530
1968	66 000	273	13 800	26 200	23 100	2 590
1969 (prel.)	69 300	257	14 000	27 400	24 800	2 970

[a]Includes commingled condensate. Beginning 1950, consumption includes petroleum products (net imports).

[b]Marketed production; includes amount stored and lost in transmission. Consumption includes dry and liquid gas. Beginning 1965, on pressure base of 101.54 kN/m^2 absolute; formerly, on base of 96.86 kN/m^2.

Table 3-4. - SPECIFIC ENERGY CONSUMPTION BY THE ELECTRIC UTILITIES IN THE BRD[3]

Year	Consumption, MJ/Kwh
1950	21.8
1960	12.8
1970	10.8
Projected	
1975	10.0
1980	9.8

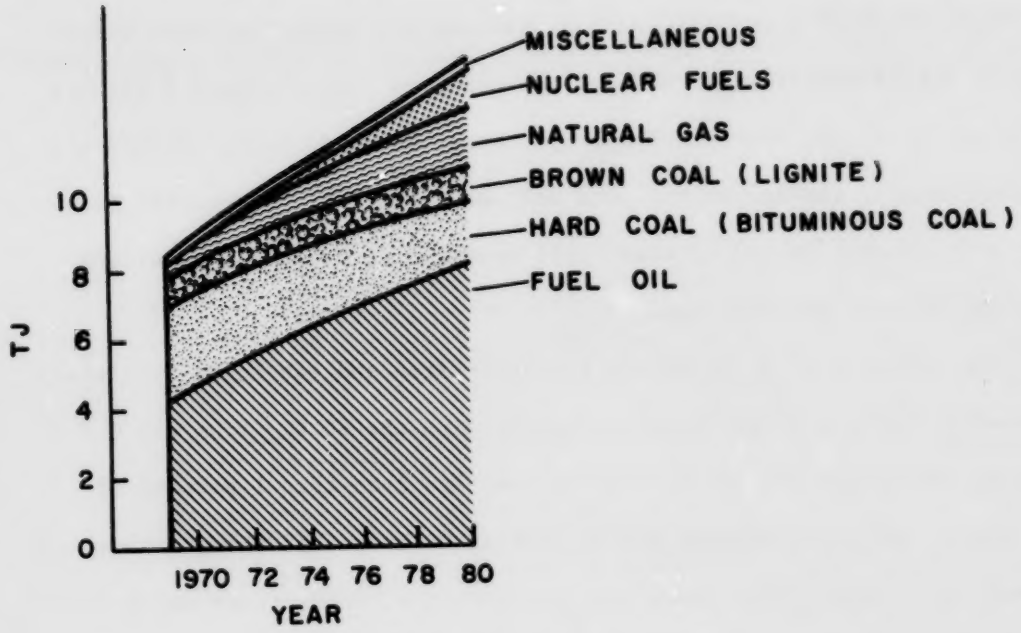


Fig. 3-1. Energy sources in the BRD projected to 1980.

fuels. The nearly 1 000 steam-electric generating plants in the United States[4] burn coal, residual fuel oil, or natural gas. Projections of U.S. power generation from various energy sources are shown in Table 3-5 through 1990. Similar data for the BRD are given in Table 3-6.

The steam boiler is the most common industrial stationary combustion device. Other types of boilers used by industry employ hot water, molten salt, organic liquids, or mercury. Fired stills, heaters, ovens, and furnaces are also used; these devices burn coal, natural gas, or petroleum-derived fuel oils. Industrial process or incineration sources that burn other fuels are included in this discussion because they are fundamentally the same as stationary combustion sources.

More than 30 million domestic and commercial space-heating plants in the United States[6] burn coal, natural gas, or petroleum fuel oil; a few burn liquefied petroleum or natural gas products. More than 2.5 million homes are heated by electrical energy. Other minor domestic sources are kitchen ranges, clothes driers, and hot water heaters. Commercial buildings are commonly heated by steam-type systems, although hot water and warm air systems are also used.

The quantity of CO emissions from oil-fired and gas-fired stationary combustion sources is negligible compared with the 90 Gkg from all U.S. sources; emissions from coal-fired sources are less than 1 percent of the total. Emission factors for estimating CO emissions from various sources facilitate qualitative, not quantitative, comparisons among various fuels and equipment. Differences in CO emissions from coal-, gas-, and oil-fired power boilers have not been proven. Probably, coal-fired stoker, or grate-type commercial, or industrial combustion equipment emits more CO

Table 3-5. - ESTIMATED U.S. POWER GENERATION FROM VARIOUS ENERGY SOURCES[4]

[In 10^{15} Joules]

Energy source	1968	1980	1990
Coal	2 460	4 410	5 870
Oil	374	738	792
Gas	1 100	1 740	2 230
Hydroelectric	800	987	1 135
Nuclear	43	3 260	11 020
Total	4 777	11 135	21 050

Table 3-6. - POWER GENERATION FROM VARIOUS ENERGY SOURCES IN THE BRD, 1970[5]

Energy source	10^{15} J	Percent of total
Coal	396.0	68
Oil	73.4	12
Gas	32.3	6
Hydroelectric	55.7	9
Nuclear	21.5	4
Miscellaneous	4.7	1
Total	583.6	100

per unit of heat input than an equivalent oil- or gas-fired unit; well-adjusted, domestic coal-fired units do emit more than well-adjusted, equivalent oil- or gas-fired units. Insufficient air supply can increase several thousand times the CO emission rate from well-adjusted units; under these conditions, oil-fired and coal-fired units emit dense smoke, but gas-fired equipment must be badly out of adjustment to emit smoke.

The BRD shows a similar pattern of CO emission sources with transportation accounting for 7.6 Gkg/yr. In some sections where coal-fired sources predominate (e.g., NRW), emissions from these sources will match those from transportation during the winter months.[7,8,9]

3.2 INDUSTRIAL PROCESS SOURCES

3.2.1 Iron and Steel Industry

Carbon monoxide is generated during several stages in the production of iron and steel: sinter plants for beneficiating iron ore emit significant amounts, and blast furnaces for producing hot metal generate large amounts but release insignificant amounts since the gases are cleaned and used as fuel; of the steelmaking furnaces, recent basic oxygen furnaces have provisions to cool and clean the offgas for use as fuel, open-hearth furnaces have excess air supplied to the end-fired burners to consume completely the CO released from the metal bath, and electric furnaces burn at the electrode ports the small amounts emitted. Coke ovens generate significant amounts, but most is collected with the coke oven gas and used as fuel. Cupolas produce significant amounts, and only a few are being controlled. Heating furnaces and boilers used in the steel mills are subject to the same emission problems as other boilers.

3.2.1.1 Iron Ore Beneficiation (Sinter Plants)--Iron ore is beneficiated by grinding, concentrating it magnetically, and sintering the concentrate

as coke or pellets for use as a burden for blast furnaces. Total U.S. plant capacity in 1960 was 59 Gkg of sinter coke and 13.5 Gkg of pellets. Capacity in 1970 was 68 Gkg of sinter and 36 Gkg of pellets.[10]

Carbon monoxide emissions from sintering operations can be estimated from Table 3-7. A typical value, 14 m^3/1 000 kg of raw sinter mix or 19 m^3/1 000 kg of finished sinter, is about 16 kg of CO per 1 000 kg of raw sinter mix or 22 kg of CO per 1 000 kg of finished sinter. Carbon monoxide emissions from firing pellets can be expected to be approximately the same. Data from the BRD reports an emission factor of 20 kg of CO per 1 000 kg of sinter.[11]

From the capacity projections, 1968 U.S. production of sinter is estimated as 67 Gkg and pellet production as 32 Gkg. From 1968 production, CO emissions are calculated to be 1.5 Gkg for sinter and 0.71 Gkg for pellets annually. CO generation in the BRD is placed at a yearly total of 0.66 Gkg from operations which produced 33 Gkg of sinter in 1971.[12]

3.2.1.2 Blast Furnaces--A blast furnace is a large cylindrical structure, approximately 30 m high, made of steel and lined with refractory brick. Iron ore, coke, and limestone are charged at the top, and heated air is blown in at the bottom. Coke, preheated by the hot gases ascending from the hearth, contacts the air of the hot blast and burns with great intensity. At the high temperatures (above 1 900 K), CO_2 is not stable because of the large quantity of carbon present as coke; thus any CO_2 formed reacts immediately with carbon (C) to form CO:

$$CO_2 + C \rightarrow 2CO .$$

In modern blast furnaces between 300 and 450 kg of carbon react in this manner for every 1 000 kg of hot metal produced.[13] This forms between

Table 3-7. - GASEOUS EMISSIONS FROM SINTERING OPERATIONS

IN THE UNITED STATES

Experiment no.	Fuel		Water, percent	Atmosphere	Specific volume,[a] m^3/1000 kg	Mean temp. of lower bed, K	Gas, percent		Composition	
	Nature	Percent					CO_2	CO	O_2, percent	CO / (CO+CO_2)
A-1	Coke--3 mm	4	3.5	Air	980	1 710	4.7	1.1	15.2	0.19
A-2	Coke--3 mm	4	3.5	Air	1 000	1 710	4.6	1.1	15.0	0.19
B	Charcoal--3 mm	3.5	3.5	Air	980	1 360	4.7	2.5	13.9	0.35
C-1	Coke--0.15 mm	4	3.5	Air	1 000	1 650	6.6	1.7	12.8	0.21
C-2	Coke--0.15 mm	4	3.5	Air	980	1 640	6.8	1.8	12.6	0.21
D	Charcoal--3 mm	3.5	3.5	O_2 9% N_2 91%	1 070	1 560	3.9	1.9	4.2	0.33
E	Graphitized electrode--3 mm	3.5	3.5	Air	1 130	1 790	4.8	0.5	15.0	0.095
F	Flue dust (16.3% C)	21.5	3.5	Air	1 180	1 520	2.5	1.05	17.5	0.30

[a]Specific volume per 1 000 kg of raw sinter mix or approximately 750 kg finished sinter.

IN THE BRD	
Sinter temperature	1 420 - 1 520 K
Exhaust gas volume analysis:	1 000 - 4 000 Nm^3/1 000 Kg (sinter)
O_2	10 - 20 volume percent
CO_2	4 - 10 volume percent
CO	0 - 6 volume percent
SO_2	0.4 volume percent

650 and 950 kg of CO. The CO reduces the iron oxides to metallic iron.

Gases leaving the furnace contain about 25 to 30 percent CO,[14] which gives the gas a heating value of about 3[illegible] kJ/m^3. Furnace gas can thus be used as fuel, but first, must be clean[illegible] remove 16 to 70 g/Nm^3 of dust. In the usual cleaning system, a dus[illegible]r (settling chamber) is followed by some type of medium-efficiency scrubber (a primary cleaner) and either a high-pressure-drop venturi scrubber, a rotary disintegrator, or an electrostatic precipitator (a secondary cleaner). A venturi scrubber is likely to be used with a blast furnace that operates at a relatively high top pressure. Part of the cleaned gas is used to preheat the blast air before its injection into the furnace through the tuyeres to intensify and speed up the burning of the coke required for smelting. For the preheating, three "stoves," or cylindrical steel vessels lined with a refractory, have an upward passage for combustion and a downward passage filled with checkerwork to absorb the heat; the three are alternately "on gas" and "on blast." Modern stoves for large furnaces are 8 to 8.5 m wide and about 37 m high.[13] The remainder of the cleaned gas is used for steam generation, heating of soaking pits, underfiring of coke ovens, and other miscellaneous heating uses.

All the CO generated in the blast furnace is normally used for fuel; abnormal conditions, however, can cause emissions of dust and CO. "Slips" are the principal problems. A slip, caused by an initial wedging or bridging of the stock in the furnace, occurs when bridged material suddenly moves downward, creates a void, and allows the gas to rush to the top of the furnace.[13] Above the bridge, the rush of gas causes abnormally high pressures--much greater than can be handled by the gas-cleaning equipment.[14]

As bleeders or safety valves open to release the pressure, a cloud of dust and CO is emitted to the atmosphere.

Practice in the BRD indicates the following analysis of top gases from blast furnaces: N_2, 55 to 60 percent; CO, 25 to 30 percent; CO_2, 11 to 17 percent; H_2, 0.5 to 4 percent; CH_4, 0 to 3 percent; and a heating value of 4.2 MJ/m^3. Gas is generated at a rate of 4.5 m^3 per kg of pig iron, a quarter of which serves to preheat the combustion air used in the hot blast stoves; another quarter drives gas power engines (dust content less than 20 $\mu kg/Nm^3$). The remaining half of the gas is used by power plants and in the coke and steel industry, but first, the gas has to be cleaned of its 10 to 50 g/Nm^3 dust load.[15]

For pig iron production in the BRD, see Table 3-8, and for blast furnace top gas production and consumption in the BRD see Table 3-9.

3.2.1.3 Basic Oxygen Furnaces--The basic oxygen process produces steel by oxidizing the impurities, principally carbon and silicon, from hot blast-furnace metal and scrap metal in an unheated, pear-shaped vessel mounted upright on trunnions. The charge, which occupies only a small portion of the vessel, is refined by a high-velocity jet of commercially pure oxygen from a water-cooled lance lowered through the vessel mouth to within a predetermined distance above the surface of the bath. The distance varies during the blow from 2 to 0.75 m in various plants.[18]

At the start of the blow, dark brown smoke evolves from oxidation of the iron and persists until the silicon, manganese, and phosphorus begin to oxidize; then these oxides enter the slag, and carbon oxidizes and evolves, chiefly as CO. An excess of air, usually mixed with the gases to burn the CO as the offgases are collected, eliminates the

Table 3-8. - BRD PIG IRON AND BLAST FURNACE FERROALLOY PRODUCTION (EXCLUDING SCRAP AND SALVAGE)[16]

(Mkg)

Year	Total	Type					
		Thomas pig iron	Steel pig iron	Foundry pig iron	Hematite and malleable pig iron	Cast iron and ferro manganese	Ferro-silicon
1955	16.5	10.6	3.7	0.9	0.75	0.24	0.33
1960	25.7	16.7	6.8	0.7	0.95	0.28	0.31
1965	27.0	14.9	9.8	0.45	1.29	0.28	0.28
1971	30.0	11.8	16.1	0.28	1.43	0.21	0.13

Table 3-9. - BRD BLAST FURNACE TOP GAS PRODUCTION AND CONSUMPTION[17]

($Nm^3 \times 10^6$)

Year	Production	Consumption						Lost and wasted
		Total	Area of use					
			Power generation	Steam boilers	Metal-lurgy	Coke ovens	Hot rolling mills	
1950	8 267	6 740	949	1 617	314	2 705	572	1 700
1960	18 448	14 021	1 168	3 371	855	5 532	2 271	3 822
1965	14 005	11 586	402	2 718	475	4 744	2 180	2 418
1971	12 614	10 574	196	3 798	553	3 990	1 411	2 041

possibility of an explosion from ignition within the exhaust system. Many furnaces are equipped with waste-heat boilers for thermal recovery from burning of the CO.[19]

From the 70:30 ratio of hot metal and scrap, plus burnt lime, the offgas will produce about 62 to 76 kg of CO per 1 000 kg of steel. After aspirated air is added to the offgas, the weight of dry gas will increase to about 900 to 1 000 kg per 1 000 kg; and after combustion, CO content will be from 0 to 1.3 kg. During the normal operation of an iron and steel plant, only small amounts of CO reach the atmosphere from this source.[19]

A typical basic oxygen process plant arrangement is shown in Fig. 3-2; gas flammability, as well as gas composition as a function of time, is given in Fig. 3-3.

3.2.1.4 Iron Cupolas--In a cupola, or vertical refractory-lined cylinder open at the top and equipped at the bottom with air nozzles (tuyeres), air from a forced-draft blower blows across alternate charges of metal, coke, and limestone placed on top of the burning coke bed. The heat generated melts the metal, which is drawn off through the tap hole.

As in the blast furnace, blowing air into an incandescent bed of coke forms a considerable amount of CO. Gases from cupolas contain from 10 to 13 percent CO.[22] This is 110 to 185 kg of CO per 1 000 kg of iron melted. A 1966 questionnaire survey by the Environmental Protection Agency and the U.S. Department of Commerce revealed that 1 680 U.S. foundries produced 13.3 Gkg of iron castings shipments in cupolas that required 29.4 Gkg of melt. Approximately 10 to 20 percent of this production was subject to flame afterburner control, which was about 90

1 Flare
2 Stack
3 Induced draft fan
4 Wastewater
5 Bucket
6 Injection water
7 Surface heat exchanger
8 Prescrubber
9 Collector
10 Converter
11 Steam drum

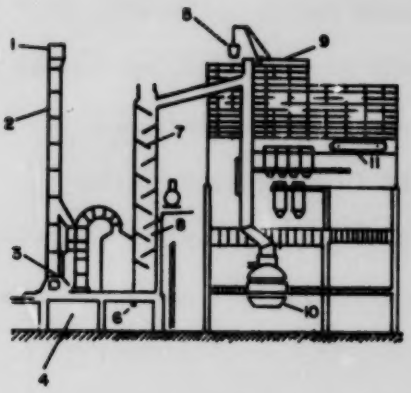


Fig. 3-2. The basic oxygen process, "LD - Blasstahlverfahren"[20]

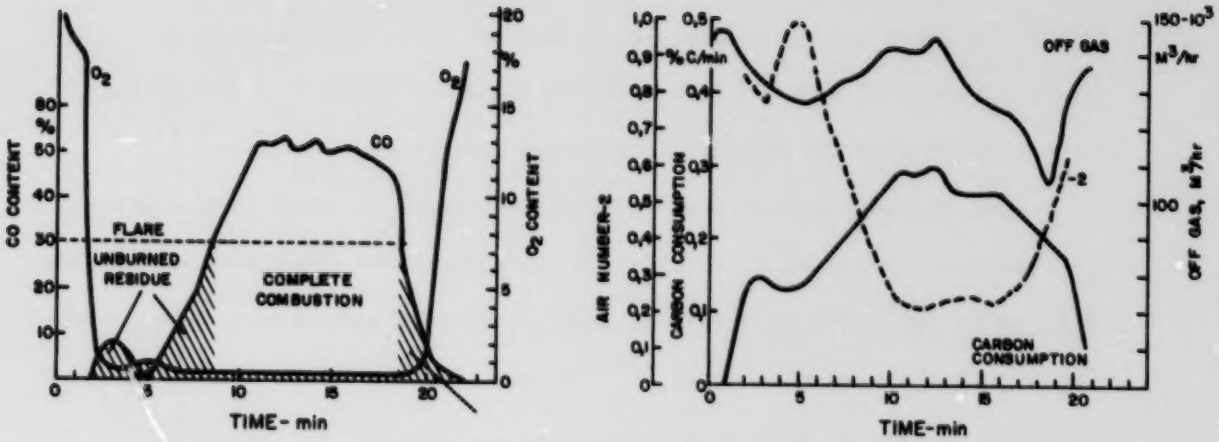


Fig. 3-3. Oxygen blast converter process cycle time[21]

percent efficient for CO reduction. With a CO emission factor of 125 kg/1 000 kg of melt for uncontrolled cupolas and 5 kg/1 000 kg of melt (or charge) for controlled cupolas, 3.14 Gkg of CO were emitted from iron cupolas in 1966 in the United States.

Test work in the BRD reports the relationship among CO content, moisture level, preheating, and afterburner application on the combustibility of cupola offgases (see Fig. 3-4). There are 1 800 cupolas in the 900 foundries in the BRD producing 2.44 Gkg of melt in 1971. Emission of CO was estimated at 150 Mkg.

3.2.1.5 Open Hearth Furnaces--The open hearth process (Siemens) does not produce CO because of the preheated excess air used with the combustion gases, the high temperature maintained in the exhaust channels, and the long blow period.[23] Figure 3-5 illustrates the furnace arrangement.

3.2.1.6 Electric Furnaces--In 1967, 13.6 Gkg, or 11.8 percent, of the U.S. steel was produced in electric-arc furnaces.[24] The electric furnace is particularly well adapted to the production of steel from cold scrap. Since the basic oxygen process has a limited scrap-handling capacity and since a plentiful supply of inexpensive scrap is available, the production rate of steel from electric furnaces continues to increase.

When excess carbon (rarely over 0.5 percent) is added to the charge, it creates a carbon boil, which stirs and purges the metal bath and yields 9 kg of CO per 1 000 kg. Perhaps half of the CO reacts with oxygen to CO_2 within the electric furnace.[25] Essentially all of the remainder oxidizes to CO_2 at the electrode ports.

The submerged arc electric furnace is used in the production of ferroalloys; Table 3-10 shows U.S. production in 1967.

Combustibility of cupola furnace gas at different moisture contents

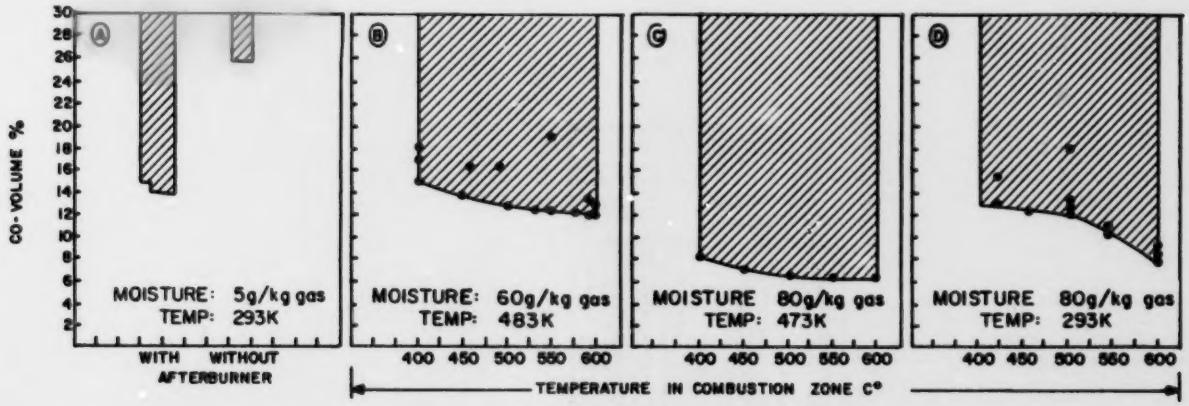


Fig. 3-4. Combustibility of gas mixtures as a function of CO content

a. Normal conditions, cold furnaces
b. With gas preheat, combustion zone without afterburner pilot flame
c. With gas preheat, with afterburner pilot flame
d. Without gas preheat, with afterburner pilot flame

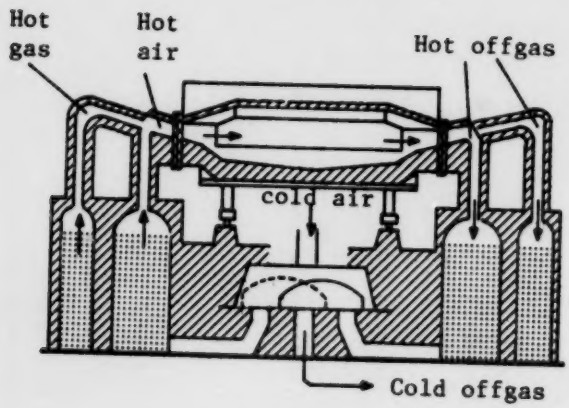


Fig. 3-5. Typical open hearth steel furnace

Table 3-10. ELECTRIC FURNACE PRODUCTION OF FERROALLOYS IN THE UNITED STATES, 1967[19]

[Mkg/yr]

Ferroalloy	Production
Ferromanganese	254
Ferrosilicon	478
Ferrochromium	238
Ferrochromsilicon	140
Ferrophosphorus	101
Silicomanganese	208
All others	235
Total	1 654

Ferroalloys are made by reducing oxides. In making ferrochromium, the charge may be chrome ore, limestone, quartz (silica), and coal and wood chips as well as scrap iron; in this case, the silica and lime would form a slag. In making ferrosilicon, the charge would be iron scrap, silica, and coke. In every case, large amounts of CO escape through the pores and channels in the charge, and the escaping gas carries large quantities of submicron particles (50 percent less than 0.1 μm), which are difficult control problems.

Offgases contain 85 percent CO, 2.5 percent carbon dioxide, 0.5 percent oxygen, 10 percent hydrogen, and 2 to 2.5 percent each methane and nitrogen. Utilization of this gas even as boiler fuel (approximate heating value, 12.7 MJ/m^3) would require scrubbing for removal of dust and would be only marginally economical. Most furnaces operate with an open top and burn the CO as it escapes through the charge. Escaping CO is normally about 670 K but may be as much as 1 090 K. Residual CO (several percent) may be caused by incomplete combustion and the high equilibrium CO concentrations at flame temperatures. Adequate ventilation in the furnace areas holds CO levels within safe limits; CO monitors warn of hazardous concentrations.

Figure 3-6 illustrates an electric arc furnace with dust control typical of the ferroalloy industry: the fan draws dilution air through the gap between furnace body and cover. (If a baghouse is used instead of a wet scrubber, dilution air is even more necessary to lower the gas temperature.) Inside the furnace cover, CO burns when it mixes with the air, and unburned CO goes through the particulate control device and up the stack. No emission factors are available for these furnaces. Wit

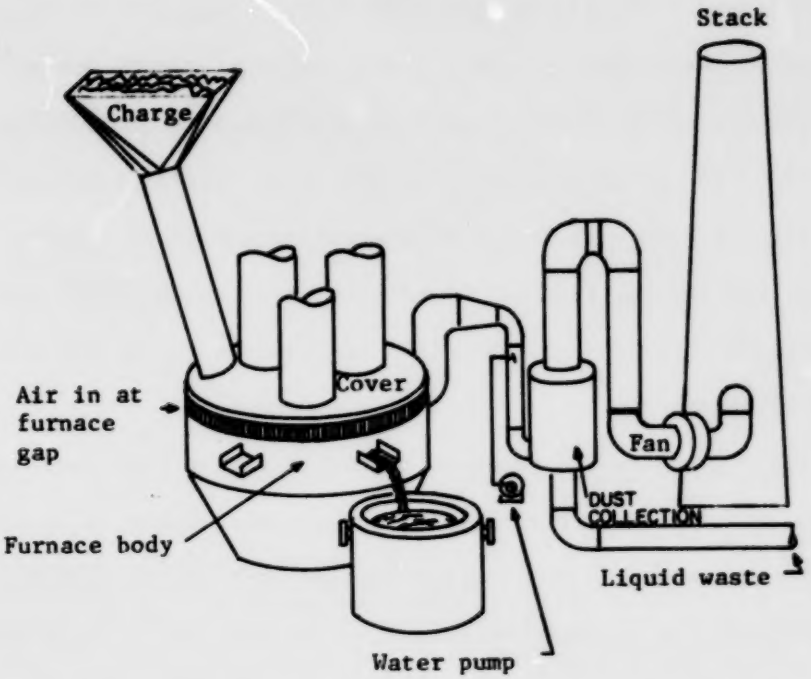


Fig. 3-6. Electric furnace for ferroalloys industry

a tight hood, the CO content of scrubbed gas will be 80 to 90 percent, and the gas can be used as boiler fuel if a user is nearby; otherwise, the gas can be flared.

Because these furnaces are extremely dusty, there will be increasing pressure in the future for particulate controls. Baghouses and other control devices would cost less if the furnace offgases could be cooled by radiation or other methods instead of by air dilution which increases the gas volume handled. This modification would require closed systems handling and emitting relatively concentrated CO, which would greatly increase CO emissions. It might be possible to use the gas as fuel or to flare it.

3.2.1.7 Coke Ovens--Coke is produced by carbonization (the destructive distillation of coal) in either beehive or byproduct ovens, both of which are carefully heated to coking temperature and kept hot for the 20- to 30-year lifetimes. A battery may consist of as many as 100 coke ovens side by side in a continuous structural unit. Annual U.S. coke production from the two types of ovens is given in Table 3-11. By 1967, production in beehive ovens had declined to about 1.2 percent.[24] BRD coke production is given in Table 3-12.

Beehive ovens are far worse air polluters than byproduct ovens. About 6 000 kg of coal per batch is charged through an opening in the dome-like roof--the same opening through which products of distillation and combustion escape; a front door is used to regulate the air admitted during coking and to discharge the finished coke. Between charges, enough heat is retained by the oven to ignite gases at the surface of the new charge and provide heat for the coking process. As heat builds up during

Table 3-11. - HISTORICAL STATISTICS OF THE U.S. COKE INDUSTRY[26]

Year	Coke production, Gkg			Production from byproduct ovens, percent	Yield of coke from coal, percent
	Byproduct ovens	Beehive ovens	Total		
1880		3.0	3.0		63.7
1890		10.4	10.4		63.9
1900	1.0	17.6	18.6	5.2	63.9
1910	6.4	31.2	37.6	17.1	66.1
1920	27.9	18.6	46.5	60.0	67.4
1930	41.0	2.5	43.5	94.2	68.7
1940	48.9	2.8	51.7	94.6	70.1
1944	60.7	6.4	67.1	90.6	70.3
1950	60.6	5.3	65.9	92.0	69.9
1955	66.7	1.5	68.2	97.7	69.9
1960	51.0	0.9	51.9	98.2	70.3
1966	59.8	1.3	61.1	97.9	69.9
1967	57.7	0.7	58.4	98.8	69.6
1968	57.3	0.7	58.0	98.8	70.2

Table 3-12. - COKE PRODUCTION IN THE BRD[27]

[Gkg]

Yield	Coal used	Coke production	Yield, percent
1950	2.82	2.16	76.4
1955[a]	4.65	3.51	75.5
1960	9.92	7.53	75.9
1965	7.17	5.39	75.2
1971	10.40	7.95	76.4

[a]Production before 1955 does not include the Saar.

coking, the coal is transformed into a pasty, semifused, expanded mass; when coking is finished and the bricks placed in the door are torn away, the coke rapidly cooled by spraying water breaks into irregular column-like pieces characteristic of beehive coke; the cooled coke is screened.

In byproduct ovens, coal is heated in the absence of air, and volatile matter is ducted to equipment that extracts valuable ingredients such as tar, ammonia liquor, and light oil from the gas. After 14 500 to 18 000 kg of coal are charged from ports in the top of the oven, the ports are sealed, and the coal begins to fuse. The fusing works toward the center from each of two walls of the rectangular oven; eventually, a crack forms down the middle of the charge where the two fused zones meet. In about 20 hours, carbonization is finished and the charge is shoved out into quench cars, cooled, and screened. The high-temperature process, 1 170 to 1 450 K, is used almost exclusively in the United States.

The hot coal gas is first cooled with an aqueous solution of ammonia to condense tar and fixed salts, such as ammonium chloride. Remaining tar is removed by further cooling and electrostatic precipitation. The ammonia is recovered by use of a weak solution of sulfuric acid. An acid separator then removes sulfuric acid mist. Liquid oil, removed in a series of scrubbing towers, is distilled and treated to yield benzene, toulene, and other products. Approximately 36 percent of the coke oven gas (heating value 20.6 MJ/m^3) produced during coking is used to heat the coke ovens;[24] the remainder is usually used for heat in other processes in the steel plant.

About 420 m^3 of coal gas is recovered from the production of 1 000 kg of coke in a byproduct oven.[26] About 6 percent, by volume, of this gas

is CO.[28] Efficient combustion of the gas, to provide heat for coking or other processes, oxidizes the CO to CO_2; but some CO emissions occur during charging and discharging.

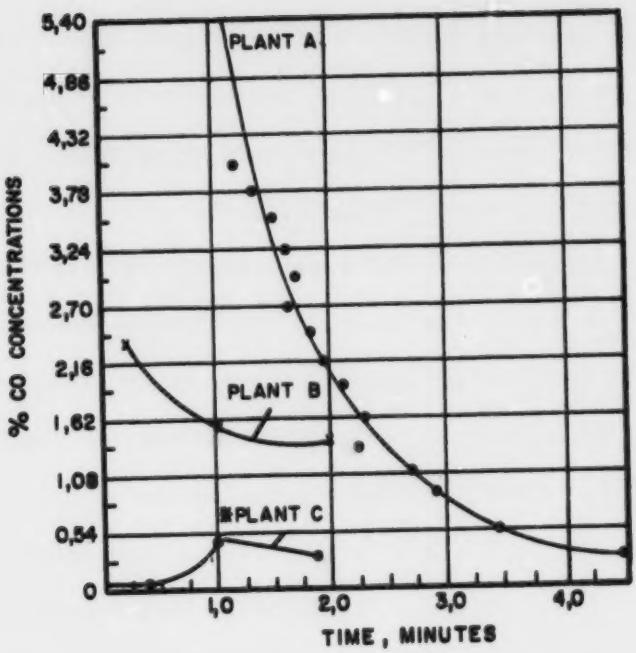
Referring to Fig. 3-7, it is noted that concentrations greater than 5.4 volume percent last no longer than one minute (Plant A). Concentration reduction is rapid when charging gas exhaust is flared (Plant C). Experience in the BRD shows CO emissions of 3 to 5 Nm^3 per 1 000 kg of coke, of which 10 percent is CO by volume. Based on operation in the BRD in 1971, 3 Mkg of CO were released to the atmosphere.

Coal gas formed inside of beehive ovens is burned inefficiently to provide heat for coking. Combustion products and unburned coal gas escape to the atmosphere. If the figures for byproduct ovens are assumed to apply to the gases escaping from beehive ovens, then CO emissions (based on 1967 coke production) from all U.S. beehive ovens would total 15.2×10^6 m^3, or 18.14 Mkg a year.

3.2.2 Petroleum Refineries

Sources of CO in a petroleum refinery include catalyst regenerators, coking operations, blanketing gas generators, flares, boilers, and process heaters. Only moving-bed catalyst regenerators and fluid cokers emit significant amounts of CO.

3.2.2.1 Catalytic Operations--In petroleum processing, catalysts are employed in the operations of cracking, reforming, hydrotreating, isomerization, hydrocracking, alkylation, and polymerization. To maintain catalyst activity and to preserve equipment, carbon deposits from coking of feed material must be periodically burned off the catalysts at a controlled temperature (below 870 K). Temperature is controlled by limiting



* PLANT C. with charging gas exhaust flare.

Fig. 3-7. CO concentrations during charging and discharging.[29]

the rate of combustion airflow. This leads to the formation of CO. Regeneration removes sulfur and nitrogen compounds. Cracking is the only operation that requires regeneration frequently enough to produce significant amounts of CO, but in some operations the catalyst particles circulate between the reaction zone and the regeneration zone and thus are continuously regenerated.

Catalytic cracking units are of two types: fluid catalytic cracking (FCC) units and Thermofor catalytic cracking (TCC) units. The FCC uses a powdered catalyst, and the TCC uses beads or pellets. In the FCC reactor, a large vertical cylinder, the bed of powdered catalyst is fluidized by the flow of vaporized feed; the regenerator, a similar vessel, may be above, below, or beside the reactor. Circulating continuously, the catalyst stream is stripped of hydrocarbon vapors by steam in the reactor and then conveyed by airflow to the regenerator where additional air is injected for the burnoff. Burnoff rates vary with the size of the unit from 0.630 to 4.28 kg/s. A stream of regenerated catalyst is continuously returned to the reactor where its sensible heat furnishes the required heat for cracking.

Regenerated catalyst and vaporized feed enter the top of the reactor chamber and travel concurrently to the bottom of the vessel where the catalyst is purged with steam before it travels by gravity into the regenerator. From the bottom of the regenerator, the catalyst is returned by an airlift (formerly by a bucket elevator) to a surge hopper above the reactor. An average-sized TCC unit regenerator has a burnoff rate of 0.442 kg/s.

Emission rates from different units show considerable variation, but average emission factors have been determined as follows: for FCC units, 39.2 kg of CO per m^3 of fresh feed; for TCC units, 10.9 kg of CO per m^3 of fresh feed.[30] A recent study gave the total 1967 rated capacity of the catalytic cracking units in the United States as shown in Table 3-13. From the preceding emission factors and capacity figures and a factor of 0.9 that relates capacity per stream-day to charge per calendar-day, the CO generated was calculated to be 6.8 Gkg per year for FCC units and 0.383 Gkg per year for TCC and Houdriflow units.

Total production from catalytic and hydrocracking units in the BRD for 1971 was 6.635 Gkg.[31] Exhaust regeneration offgas from these units contains 6 to 8 volume percent of CO which is generally flared.[32]

3.2.2.2 Fluid Cokers--A fluid-coking unit resembles an FCC unit in that a bed of fluidized solids is used to transfer heat to the partially vaporized feed material. It differs in that the solid particles are coke, a product of the cracking.

A thin liquid film of circulating, fluidized, seed coke is agitated at 750 to 840 K by rising gaseous products in the reactor.[33] A stream of coke particles is continuously withdrawn, steam-stripped, and transported to a burner, where the coke bed is maintained at 870 to 920 K. A stream of coke at this temperature is returned to the reactor. More coke is formed in the reactor than is burned; consequently, a coke-product stream is withdrawn. Because coke is burned under conditions of limited air, with respect to the amount of carbon present, the flue gas is rich in CO.

Table 3-13. - CATALYTIC CRACKING CAPACITY IN THE UNITED STATES

Type of unit	Total feed, m^3/stream day	Recycle, percent
FCC	729 000	29.9
TCC	120 000	29.0
Houdriflow	31 800	29.2

The CO emissions average 85 kg/m^3 of fresh feed.[34] In 1960, the total capacity of U.S. fluid coking plants was 16 000 m^3/day.[35] On this basis, the total CO was 0.5 Gkg/yr. Estimated CO emissions (Table 3-1) indicate that boilers are often used to burn the CO generated in fluid coking.

3.2.3 Chemical Industry

Carbon monoxide may be used as a raw material for synthesizing chemicals such as methanol and phosgene. It is also produced as a byproduct in the manufacture of synthesis gases (hydrogen or a mixture of hydrogen and nitrogen). In the case of phosgene, CO is either removed or, more commonly, oxidized to CO_2 or reduced to methane.

Some CO is generated in the air oxidation of hydrocarbons to produce maleic acid, phthalic acid, terephthalic acid, and cyclohexanol.[36]

Table 3-14 compares various industrial gases by content of CO and hydrogen; the last three are raw, unpurified synthesis gases. Steam-reforming of methane is favored in the United States where there is a plentiful supply of cheap natural gas.[37] Partial oxidation is more often used in Europe.

Estimated production of CO by the chemical industry of the United States is somewhat greater than 6 Gkg/yr.

Most of the CO generated by chemical plant operations in the BRD comes from the production of formaldehyde and carbon black, about 80 Mkg annually.

3.2.3.1 Synthesis Gas--Most of the hydrogen (H_2) used by the U.S. chemical industry is made by steam-reforming; natural gas (C_nH_m) is the hydrocarbon source most often used. This reaction for generating syntehsis gases for

Table 3-14. CARBON MONOXIDE AND HYDROGEN CONTENT OF SOME INDUSTRIAL GASES IN THE UNITED STATES

[Volume percent]

Gas	CO	H_2
Coke oven	6.3	53
Blast furnace	27.5	
Water gas	42.8	49.8
Methane reformer	15.5	75.7
Methane partial combustion	35.6	61.5
Oil partial combustion	47	47

products such as methanol and ammonia and for manufacturing hydrogen necessarily involves the generation and handling of CO. The basic general reaction is

$$C_nH_m + nH_2O \rightarrow nCO + \frac{2n+m}{2}H_2 .$$

This general reaction applies to methane as follows:

$$CH_4 + H_2O \rightarrow CO + 3H_2 .$$

The reaction is favored by high temperature and low pressure, but modern plants operate at pressures of 3.1 MN/m^2 (gauge) or more, for economic reasons, and the gas reformers (furnaces having alloy tubes containing a nickel-base catalyst) usually operate at 1 030 to 1 260 K.[37] The gas most often needed is hydrogen. After steam-reforming, the CO can be removed by the water-gas shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2 ,$$

and the CO_2 is removed by scrubbing. This reaction is not affected by pressure, but is favored by low temperatures which reduce the reaction rate. Highly active low-temperature catalysts (under 530 K) remove most of the CO at a reasonable rate in one shift stage. Small residual amounts of CO and CO_2 can be removed by methanation:

$$3H_2 + CO \rightarrow CH_4 + H_2O .$$

This reaction is carried out at elevated temperatures over a nickel catalyst and can reduce CO to less than 10 ppm.[37]

In another type of reforming, hydrocarbons (e.g., naphtha or natural gas) are burned under reducing conditions:

$$C_nH_m + \frac{n}{2}O_2 \rightarrow n\,CO + \frac{m}{2}H_2 .$$

The percentage of CO in the raw synthesis gas increases with the C:H ratio of the hydrocarbon. Typical results with 95 percent pure oxygen as the oxidant are given in Table 3-15.

3.2.3.2 Methanol--Synthesis gas can be produced for use directly in methanol synthesis without the separations or adjustments required for making phosgene, ammonia, and other products. Theoretically, the 1968 production of synthetic methanol in the United States, about 1.7 Gkg,[39] would require a feed of 1.5 Gkg of CO, the minimum known requirement for this production. The 1970 production of methanol in the BRD was 0.876 Gkg.[40] Methanol (CH_3OH) is synthesized as follows:

$$CO + 2H_2 \rightarrow CH_3OH .$$

This reaction, favored by high pressure and low temperatures, is exothermic. Pressures of 31 MN/m^2 (gauge) and temperatures up to 650 K have been used with a suitable catalyst; methanol converters of some modern plants use new copper-based catalysts permitting operations at 4.8 MN/m^2 (gauge) and 530 K.[41] Temperature control is by dilution with quench gas or carbon dioxide. Impurities are removed by flashing on pressure letdown, followed by distillation. Unreacted gas is recycled by the compressor and combined with fresh feed; inert gases are purged to prevent them from building up.

Table 3-15. - SYNTHESIS GAS COMPONENTS IN THE UNITED STATES[38]

[Volume percent]

Synthesis gas	H_2	CO
Natural gas	60.9	34.5
Naphtha	51.6	41.8
Heavy fuel oil	46.1	46.9

3.2.3.3 Ammonia--The production of ammonia in the United States in 1968 was about 11.3 Gkg.[39] The CO required could be over 3.6 Gkg if the ammonia synthesis gas were made by the steam-methane reforming process.

The 1970 production of ammonia in the BRD was about 1.8 Gkg.[40]

For ammonia manufacture, the CO is removed by the gas shift and methanation reactions described above to a residue of less than 20 ppm because in higher concentrations it poisons the catalyst.

Ammonia (NH_3) is synthesized by the following reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3 .$$

This reaction is favored by high pressure and low temperatures; 10 to 100 MN/m^2 and 670 to 760 K have been used. In order to secure the required nitrogen-hydrogen mixture, a hydrocarbon gas is reacted in two stages: In the first stage, part of the gas is reformed with steam; in the second, the unreacted gas is partially oxidized with sufficient air to yield the proper hydrogen-nitrogen ratios.

3.2.3.4 Phosgene--Phosgene ($COCl_2$) is made from CO and chlorine (Cl_2):

$$CO + Cl_2 \rightarrow COCl_2 .$$

This exothermic reaction is carried out in water-cooled tubes filled with activated-carbon catalyst with a slight excess of CO to insure complete reaction of the chlorine. Yields exceed 99 percent.

In 1967 there were 17 phosgene manufacturers in the United States[42] with a combined capacity of over 0.36 Gkg, much of which was for in-plant use only. Theoretically, 0.107 Gkg of CO are required to make that quantity.

The CO manufacturing system for phosgene is similar to that required for making methanol in that it has a reformer; it differs, however, in that it requires relatively pure, hydrogen-free CO. A typical plant flow sheet is shown in Fig. 3-8. The CO in raw synthesis gas is purified by absorption and desorption or by cryogenic methods. A common method involves high-pressure absorption of CO in a special liquor of cuprous and cupric chlorides and ammonium carbonate:

$$Cu_2(NH_3)_4^{--} + 2CO + 2NH_3 \rightarrow Cu_2(NH_3)_6(CO)_2^{--} .$$

The absorbed CO is liberated on release of pressure. Absorption is carried out at near ambient temperature, and the temperature is raised to aid desorption. In this complicated system, the ratio of cupric to cuprous copper must be held to a certain range, and carbon dioxide and sulfides should be removed.[44] Removal is done ahead of the copper-liquor system by first passing the gases through an ethanolamine absorber-stripper system and then using cool mono- or diethanolamine to absorb the acidic hydrogen sulfide and carbon dioxide. Heating the amine solution in a stripping tower regenerates it. Phosgene manufacture may require three CO-handling units: the reformer, the ethanolamine absorber-stripper unit, and copper-liquor CO absorption-purification equipment. Nevertheless, the relatively small usage of phosgene relegates this industry to one of minor potential CO emissions.

Phosgene is such a dangerous material--so hazardous to life--that leaks anywhere in the phosgene system cannot be tolerated.

3.2.3.5 Organic Acids[45]--Carbon monoxide reacting with certain alcohols or unsaturated hydrocarbons forms organic acids. Perhaps the most

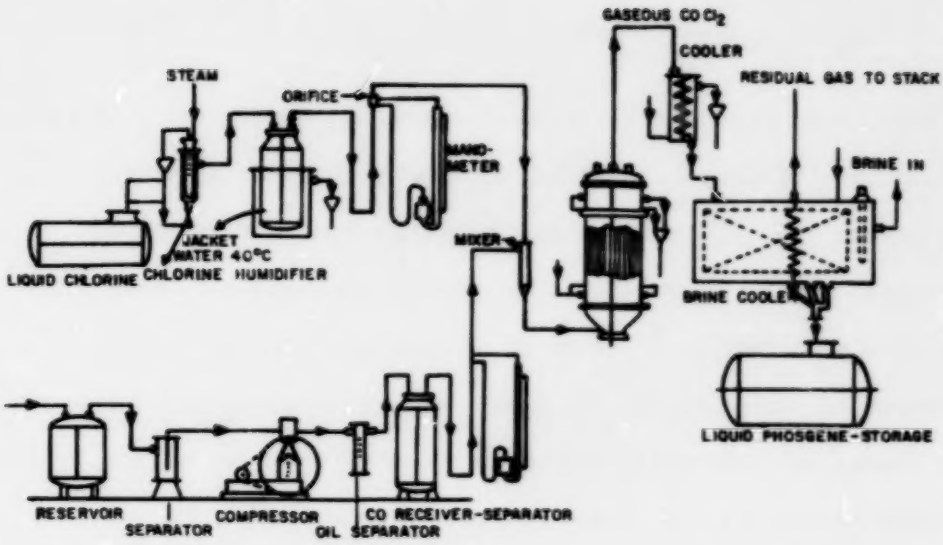


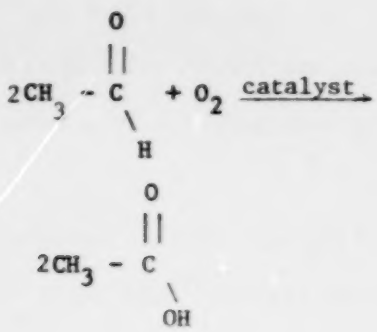
Fig. 3-8. The production of phosgene[43]

important reaction is the synthesis of acetic acid (CH_3COOH) from CO and methanol (CH_3OH):

$$CH_3OH + CO \rightarrow CH_3COOH .$$

The synthesis takes place in the presence of aqueous cobaltous iodide at about 520 K and 680 MN/m^2.[46] At one large plant CO requirements are 19 Mkg a year, exclusive of that required for making methanol.[46] Vent gases are expanded to about 1.03 MN/m^2 (gauge) and washed with methanol feed before being piped to the fuel supply. Byproducts other than gas are separated from the acid by distillation.

Another route to acetic acid is through catalytic oxidation of acetaldehyde:



Other types of organic acids (RCH_2CH_2COOH) can be synthesized:

$$RCH = CH_2 + CO + H_2O \rightarrow RCH_2CH_2COOH .$$

Acrylic,[46] pivalic,[47] succinic,[48,49] and monobasic unsaturated acids[46] are a few.

3.2.3.6 Aldehydes--Carbon monoxide reacts with certain olefins (-C=C-) to form aldehydes (-CHO). Among patented processes are the following:

$$C_2H_4 + CO + H_2 \rightarrow C_2H_5CHO .$$

At 4.13 MN/m^2 and 400 K with a catalyst of cobalt on kieselguhr, the yield of propionaldehyde (C_2H_5CHO) is over 75 percent.[50] Normal butyraldehyde (C_3H_7CHO) is formed with cobalt naphthenate at 425 K and 3.5 MN/m^2:[51]

$$C_3H_6 + CO + H_2 \rightarrow C_3H_7CHO .$$

The Oxo process is of commercial importance, especially in Europe; aldehydes can be made from olefins, CO, and hydrogen:[46]

$$RCH = CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO .$$

Olefin conversion is over 95 percent. At about 420 K and 25.4 MN/m^2 with a cobalt catalyst, some byproducts are formed which must be separated by distillation. Alcohols are made by hydrogenation in a separate process step.

Formaldehyde (HCHO) manufacture consumes about 40 percent of all the methanol produced annually in the United States.[39] Methanol vapor and air are passed over a hot catalyst at 100 kN/m^2, and the gases are absorbed in water. The following reactions may occur, depending on the type of catalyst:

$$CH_3OH \rightarrow HCHO + H_2 \text{ and } CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O .$$

Since HCHO is thermodynamically unstable, it tends to decompose under the reaction conditions into CO and H_2. Some CO is always formed. The product gases go directly to the scrubbers; CO leaves in the scrubber offgas.

3.2.3.7 Other Organic Compounds--A number of organic syntheses with CO have been worked out or patented. At least one plant abroad makes butanol (C_4H_9OH) as follows:[46]

$$C_3H_6 + 3CO + 2H_2O \rightarrow C_4H_9OH + 2CO_2 .$$

Reaction conditions are 370 K and 1.54 MN/m^2 (gauge) with a catalyst mixture containing iron pentacarbonyl. Byproducts (propane, CO_2, and hydrogen) are bled off, along with some CO, through a scrubber. Most of the CO is recycled to the reactor.

The versatile, powerful solvent, dimethyl formamide ($(CH_3)_2NO\ CH$), can be made by the following reaction:[52]

$$(CH_3)_2NH + CO \rightarrow (CH_3)_2NO\ CH .$$

This reaction requires a temperature of about 330 K, a pressure of 0.6 MN/m^2, and a sodium methylate catalyst.

Diethyl ketone ($C_2H_5\ CO\ C_2H_5$) can be made by a reaction involving CO:[53]

$$2C_2H_4 + CO + H_2 \rightarrow C_2H_5\ CO\ C_2H_5 .$$

But the yield is only 20 percent.[45]

The preceding discussion indicates that CO is an important petrochemical feedstock. Its use may greatly increase in the future. It is available in enormous amounts in the steel industry: 82 Gkg/yr from pig iron blast furnaces and 2.1 Gkg/yr from basic oxygen furnaces. A variety of synthesis gases could be made from these gases using steam and hot coke.

All CO emissions in the chemical process industry come directly or indirectly from processes involving synthesis gas, which always contain inert gases. As the reactive gases are consumed, inert gases build up, but they are commonly purged from the system by continuously bleeding off a small percentage of the total gas stream. The reacting gas is a considerable percentage of the purge stream; if the reacting gas is CO, the purge is a potential source of CO. One leading manufacturer estimates that CO emissions--including those from purging--range from 0.1 kg/1 000 kg of methanol produced in a modern single-line plant to 7.5 kg/1 000 kg in a relatively old multiple-line plant.[54] If 70 percent of the 1968 methanol was produced in modern single-line plants, total CO emissions would have been less than 3.6 Mkg. In addition to the above emissions, a 0.55 Mkg-per-day methanol plant may vent (from high stacks during several hours of startup, shutdown, or circuit upset) a mixture of the H_2 and CO containing about 4.7 Nm^3/s.

The CO emissions are about 0.05 kg/kg of formaldehyde produced.[54] Based on 1967 production figures, CO emissions amounted to 31 Mkg. The 1970 emission quantity for the BRD was 21 Mkg.

Carbon monoxide is not easy to burn; thus emissions often are released when it is used as fuel or when it is incinerated.[55,56] The lower and upper flammability limits are 12.5 and 74 percent by volume.

Leaks, a source of emissions and economic loss, are a continuous problem to engineering and maintenance.[57] Leaks occur from shaft seals, such as the stuffing boxes for agitators and pumps, and at fan and compressor shafts; valves can leak from stem-packing or faulty seating; flanges and gaskets develop leaks, especially if all of the loading conditions were not investigated during design.

Operation of safety valves may release large amounts of CO for a short time, and poor reseating of the blown valve can prolong the emission. Discs, sometimes installed to protect equipment from overpressure, release all the gas in a given system if ruptured. Both the valves and the discs are usually manifolded to a relief system having a flare or stack. A line break releases gas directly to the atmosphere.

On high-pressure systems operating near atmospheric pressure, CO and other gases may be released at a temporarily high rate through water seal pots.

3.2.4 Carbon Black Manufacture

The U.S. carbon black industry has grown 4 percent a year[58] from 1945 through 1965. At the end of 1967, the industry's nine producers had 35 plants with a production capability of 1.42 Gkg/yr.[59] Actual 1967 production totaled 1.13 Gkg. In 1968, two more large plants were put in operation; each has a capacity of 45.4 Mkg/yr.[60,61]

Production in the BRD of carbon black was 240 Mkg in 1970 and 260 Mkg in 1971.[62] About 90 percent of the carbon black is produced by the oil-furnace process (rubber industry). Other processes used for the paint and ink industries are flame-black process, DEGUSSA-CK process, electric arc process, and acetylene black process.[63]

About 93 percent of the carbon black produced is used in the rubber industry to reinforce rubber (to provide abrasion resistance to retard wear in products such as tires). In the paint and ink industries, it is a colorant. It has other uses in the food, plastics, and paper industries.

Carbon black is produced by the partial breakdown of certain hydrocarbons, by thermal cracking (thermal process), or by incomplete combustion (furnace and channel processes). All of these processes can produce CO.

In the United States, 6 percent of the carbon black is produced by the channel process, 12 percent by the thermal process, and 82 percent by the furnace process. Figure 3-9 is a flow diagram of a carbon black plant operation. CO can be emitted from leaks in the cyclones, bag filter, exhaust system after the fan, or from connecting ductwork. Some CO trapped between carbon black particles might escape in the grinder or in storage, but the amount would be minor compared to that from the exhaust system.

3.2.4.1 Channel Black--Channel black is produced by impinging a natural gas flame on a relatively cool iron plate or channel. Because the distance between the gas tip and the channel is too short to allow complete combustion, unburned carbon is deposited on the channel. Made continuously in "hot houses" containing 2 000 to 4 000 flames, the black is automatically scraped from the moving channels and conveyed to the product-handling system. Each hot house uses 4 300 to 7 400 m^3 of natural gas a day.[64] Each maintains about 810 K because of the natural draft in the building. The yield of carbon black is about 0.04 kg/m^3 of gas.[64] Recently, because of the rising cost of natural gas, the gas has been enriched with cracked recycle and distillate oil. The yield from these oils is about 120 kg/m^3.

The CO is emitted directly to the atmosphere from the hot houses; therefore, there is no practical method for accurately determining the amount. All of the CO produced is released as CO because it does not oxidize readily at process conditions. A gross estimate of CO emissions is 54.5 Mkg/yr.[64]

3.2.4.2 Thermal Black--Thermal black is produced by the decomposition of natural gas in the absence of air or flame. The checkerwork furnace is

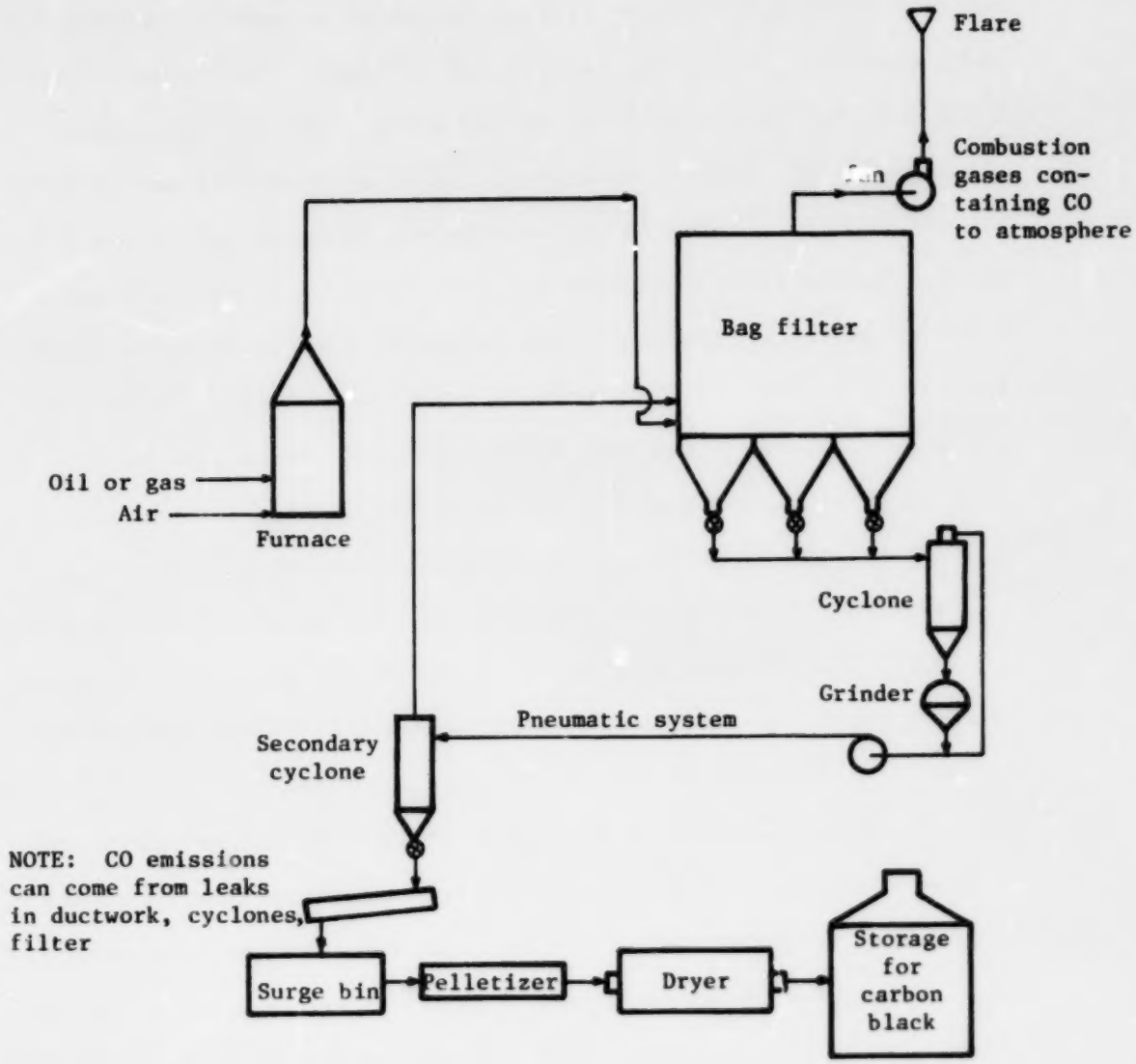


Fig. 3-9. Typical diagram for carbon black manufacture

heated to 1 590 to 1 800 K, the flue is closed, and the natural gas is admitted to the generator where it is decomposed to carbon, hydrogen, and small quantities of CO, CO_2, methane, and nitrogen. The thermal carbon black from the furnace is cooled and collected. The full cycle takes about 10 minutes, with the time being divided about equally between heating and cracking.[64] When the furnace becomes cool, the gas is shut off and the furnace is reheated with the gases (principally hydrogen) produced in the cracking process. Theoretically, 0.505 kg of carbon black and 2 m^3 of hydrogen would be produced per m^3 of methane if the natural gas is all methane. The actual yield is 40 to 50 percent (up to 0.254 kg/m^3 of natural gas).[64] Thermal black is coarse and does not have the reinforcing properties or color of channel black.

Emissions of CO are estimated at 24 kg/1 000 kg of thermal black or 3.2 Mkg/yr from the thermal process. Since the gas given off during the cracking process is used to reheat the checkerwork, much of this CO may be further oxidized to CO_2 during the reheating phase.

3.2.4.3 Furnace Black--Furnace black is produced by the incomplete combustion of fuel (oil or gas) in a specially designed furnace. At 1 480 K, the ratio of air to natural gas (4.5:1) does not allow complete combustion, and results in the production of black; after the black leaves the furnace, it is cooled, agglomerated, and collected. The yield is 25 to 30 percent for the larger particles and 10 to 15 percent for the smaller particles.[64]

Sometimes the gas is enriched with oil. The oil is preheated to 560 to 650 K; then the air and gas are fed at a constant ratio, and the weight of oil is varied to keep the furnace at 1 650 K. Different grades of

black can be produced by varying the temperature and velocity in the furnace or the geometry of the furnace. A yield of 55 percent can be expected.[64] Oil furnace black tends to predominate in the industry because of advanced technology and the increasing cost of gas.[58]

Carbon monoxide emissions vary from 5 to 11 percent by volume in the exit gases and average 0.28 kg/kg of furnace black produced.[64] This is estimated as 259 Mkg/yr of CO from the production of furnace black.

Emissions in the BRD are about 40 Mkg CO generated by the furnace process (emission factor controlled of 0.20 kg/kg of black).

3.2.5 Pulp and Paper Industry

Carbon monoxide emissions from kraft pulp mills are often overlooked. Potential sources are recovery furnaces and lime kilns. Bark-fired and fossil fuel fired boilers, other potential sources, are discussed in Section 3.1, "Stationary Fuel Combustion Sources."

3.2.5.1 Recovery Furnaces--All kraft pulp mills use one or more furnaces to recover valuable chemicals and heat energy from the black liquor produced in the wood digestion process to prevent waste disposal problems and economic losses. For example, reduction of the sodium sulfate in the liquor to sodium sulfide[65] produces a soluble sodium ion for the lime causticizing process in lime kilns.

Estimated CO emissions from U.S. kraft recovery furnaces are 635 Mkg/yr,[66,67,68] or 0.03 kg/kg of pulp produced.[66,68] An individual furnace may emit up to 2 percent when insufficient air is supplied or a negligible amount with sufficient air.[69] In other words, reducing conditions form much CO which would escape if additional air were not admitted above the reducing zone to oxidize CO. Thus if the furnace is operated as designed, very little CO is emitted.

3.2.5.2 Lime Kilns--All kraft pulp mills use one or more lime kilns to regenerate lime from calcium carbonate produced in the causticizing process. Emissions of CO from lime kilns are estimated at 118 Mkg/yr. Emission rates are estimated at 5 kg/1 000 kg of pulp produced.[67]

BRD emissions from lime kilns are estimated at 3 Mkg in 1970 (4.54 kg/1 000 kg of pulp). Production in 1970 was 560 Mkg of pulp and 5 Gkg of paper in 13 plants.

3.2.6 Miscellaneous Industrial Sources

3.2.6.1 Silicon Carbide Furnaces--Silicon carbide (SiC) is an abrasive manufactured by heating a mixture of sand (SiO_2) and coke (C) to about 2 470 K in an electric resistance furnace (Fig. 3-10). The reaction proceeds as follows:

$$SiO_2 + 3C \rightarrow SiC + 2CO .$$

Heat is generated by the resistance of the charge to a flow of electric current. The walls of the furnace are temporary; they can be torn away from the charge after completion of heating. The gases work their way out of the porous charge and escape to the atmosphere. Because the surface of the charge is relatively cool, some CO may escape unburned.

For every kg of silicon carbide formed, 1.4 kg, or about 1.12 m^3 of CO, is formed. Although much of the released CO burns above the furnace, the combustion is uncontrolled and, undoubtedly, a considerable portion dissipates into the ambient atmosphere. Silicon carbide furnaces are not normally hooded for collecting CO or for providing excess air to dilute CO concentrations

SiC production in the BRD in 1970 was about 30 Mkg.

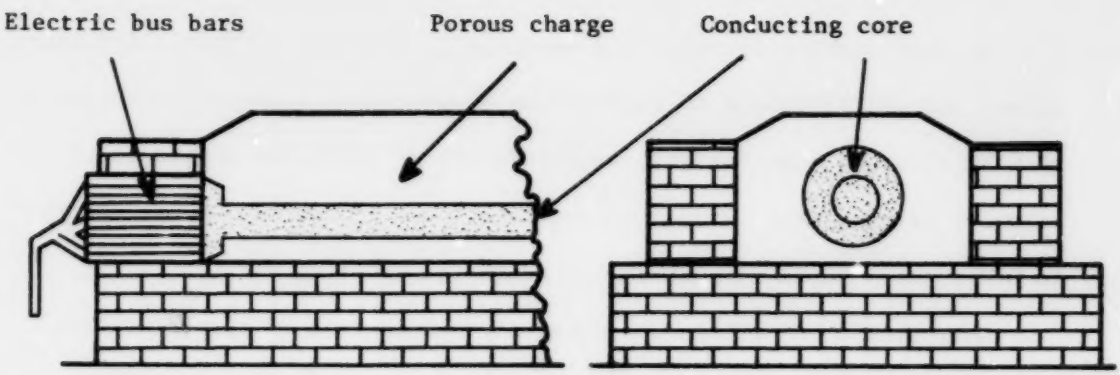


Fig. 3-10. Electric furnace for production of silicon carbide

3.2.6.2 Calcium Carbide Furnaces--Calcium carbide (CaC_2) is manufactured when solid carbon (C) reacts with liquid lime (CaO) in the melt below the electrode tips of an electric arc furnace. The reaction proceeds at about 2 370 K:

$$CaO + 3C \rightarrow CaC_2 + CO .$$

The gases that are formed escape through the porous charge. High-grade raw materials are necessary because few impurities are eliminated in manufacture. Either metallurgical coke, petroleum coke, or anthracite coal is the source of carbon. Liquid calcium carbide is removed from the bottom of the furnace.

Calcium carbide furnaces are essentially the same as ferroalloy furnaces, and may be hooded to collect the CO evolved. Because the offgas must be cleaned, even for utilization as boiler fuel, the economics of recovery is marginal. Adequate ventilation and monitoring are necessary to prevent hazardous concentrations of CO in operating areas.

Competitive combustion processes for manufacture of acetylene have largely supplanted calcium carbide as a source material for acetylene. The further burden of investment and expense for pollution control is probably not recoverable by increasing calcium carbide prices.

Calcium carbide production in the BRD in 1970 was about 900 Mkg.[70]

3.2.6.3 Elemental Phosphorus Furnaces--All elemental phosphorus is made by an electric furnace process: A mixture of phosphate rock, sand, and excess coke is heated in a three-electrode (three phase) furnace to about 1 770 K at or slightly under atmospheric pressure (Fig. 3-11). The following equation represents the overall reaction:

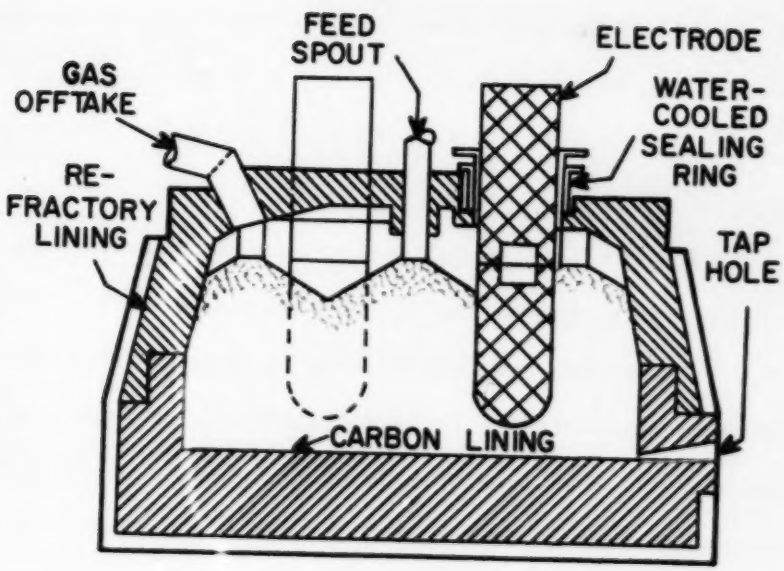


Fig. 3-11. Diagram of electric furnace for production of elemental phosphorus

$$4\,Ca_5F(PO_4)_3 + 18\,SiO_2 + 30\,C \rightarrow 18[CaO \cdot SiO_2 \cdot 1/9\,CaF_2] + 30\,CO + 3\,P_4 .$$

Excess carbon is necessary to reduce iron, which may be in the charge, and a small amount of silicon.[71] Escaping gases are primarily CO, but they do contain all of the undesirable P_4 (gas), some dust, and some SiF_4 (gas); dust is removed in an electrostatic precipitator, after which the P_4 is condensed to a liquid (m.p. 320 K) in a water condenser. Residual gas is about 90 percent CO; the balance is hydrogen, oxygen, and methane. This gas is either burned as fuel in phosphate-rock-drying kilns or flared if the kilns are out of service. The CO emissions would, therefore, be either accidental and temporary or the result of imcomplete combustion of the washed gas.

In the BRD "SODERBERG" electrodes are used instead of carbon electrodes as in the United States. Figures 3-12 and 3-13 show the construction of the cylinder which is filled with a special mass (anthracite, coke, and tar pitch).[72]

3.2.6.4 Aluminum Reduction Cells--Aluminum is produced from bauxite ore by electrolysis of alumina (Al_2O_3) dissolved in a bath of molten cryolite (Na_3AlF_6). Impurities are removed from the ore to avoid deposition in the metallic aluminum; cryolite renders the bath electrically conducting; small amounts of other fluorides lower the melting point so that the cell can operate at about 1 220 K; metallic aluminum separates at the carbon cathode, and oxygen is released at the carbon anode. Depending on the operating conditions in the cell, between 250 and 600 kg of CO is formed per 1 000 kg of aluminum produced.[68] For a 1968 production of about 2.9 Gkg of aluminum, 0.72 to 1.7 Gkg of CO were formed in the United States. Much of the CO burns upon exposure to the atmosphere or in the afterburner of cells so equipped.

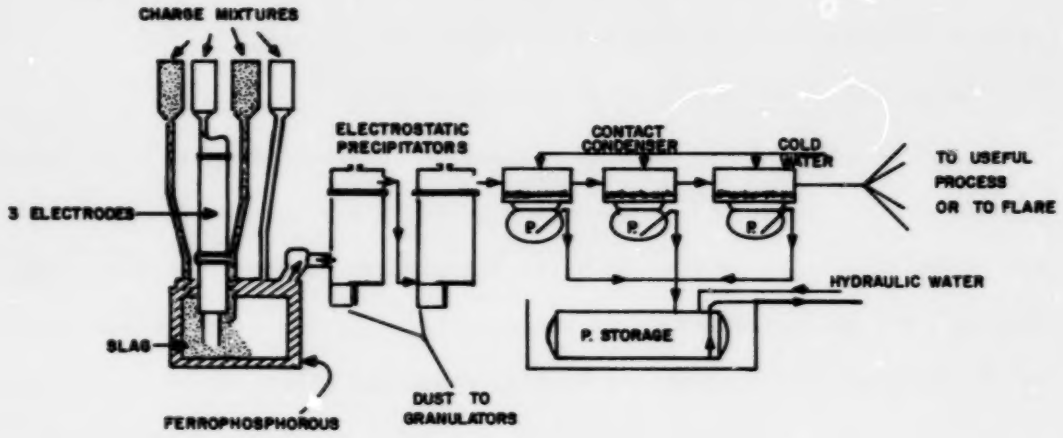
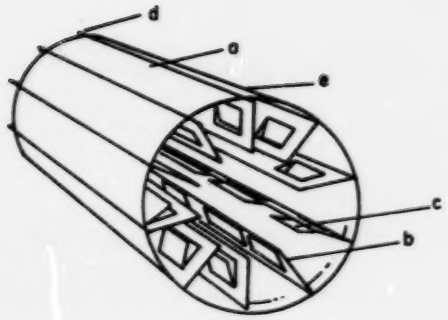


Fig. 3-12. Söderberg phosphorus furnace



a Casing
b Ribs
c Window
d Projecting rib
e Opening flap

Fig. 3-13. Cylindrical casing for Söderberg electrode

Production in the BRD was 0.309 Gkg of aluminum in 1970. The Soderberg furnace shown in Fig. 3-13 uses horizontal electrodes and is totally enclosed to permit gas exhaust and control. CO emissions in primary aluminum production are 0.120 kg/kg of aluminum.

3.3 WASTE INCINERATION AND OTHER BURNING SOURCES

Figures 3-14 through 3-20 show types of incinerators. In a multiple-chamber design (Fig. 3-16), combustion products are formed by underfire air contacting waste on the grates in the primary chamber; in the mixing chamber, gas phase combustion is promoted by admitting overfire air (up to 50 percent excess) above the burning waste and sometimes by installing auxiliary burners to supply from 1 030 to 1 250 K. Gases from the primary chamber flow to a small mixing chamber and then to a larger, secondary chamber where more complete oxidation occurs. Size and configuration vary with the service for which they are designed.[73,74]

Preliminary results of a survey by the U.S. public Health Service indicate that household, commercial, and industrial solid-waste production per capita is about 0.45 kg/day and 320 Gkg/yr nationally. About 170 Gkg/yr (or 2.4 kg/day per capita) is collected for disposal; the remainder is either disposed of onsite or handled by the household or establishment itself.[75] An estimated 160 Gkg is burned in the open or in incinerators.[76]

An additional 500 Gkg of agriculture waste and 1 Tkg of mineral wastes are generated each year.[75] About half of the agricultural wastes is burned in the open. Except for the estimated 43.5 Gkg/yr of coal refuse consumed by fire, no other mineral wastes are burned; forest-burning and structural fires consume about 200 Gkg and 7.2 Gkg/yr, respectively.[76]

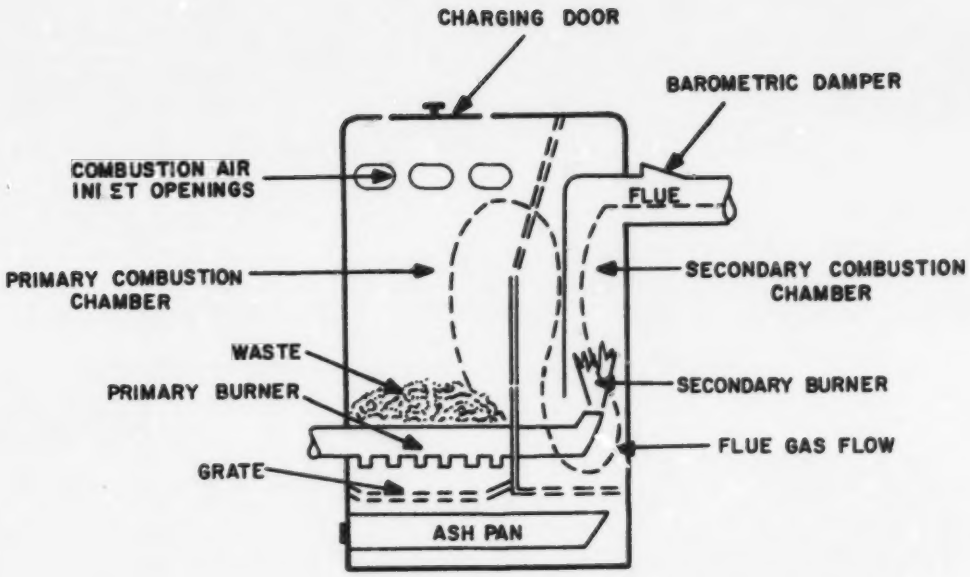


Fig. 3-14 Domestic gas-fired incinerator.

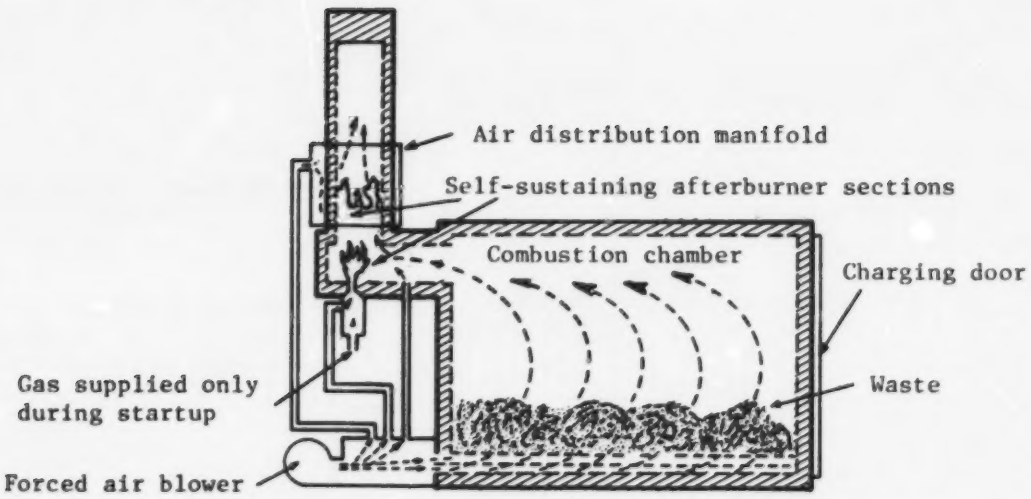


Fig. 3-15. Single-chamber incinerator

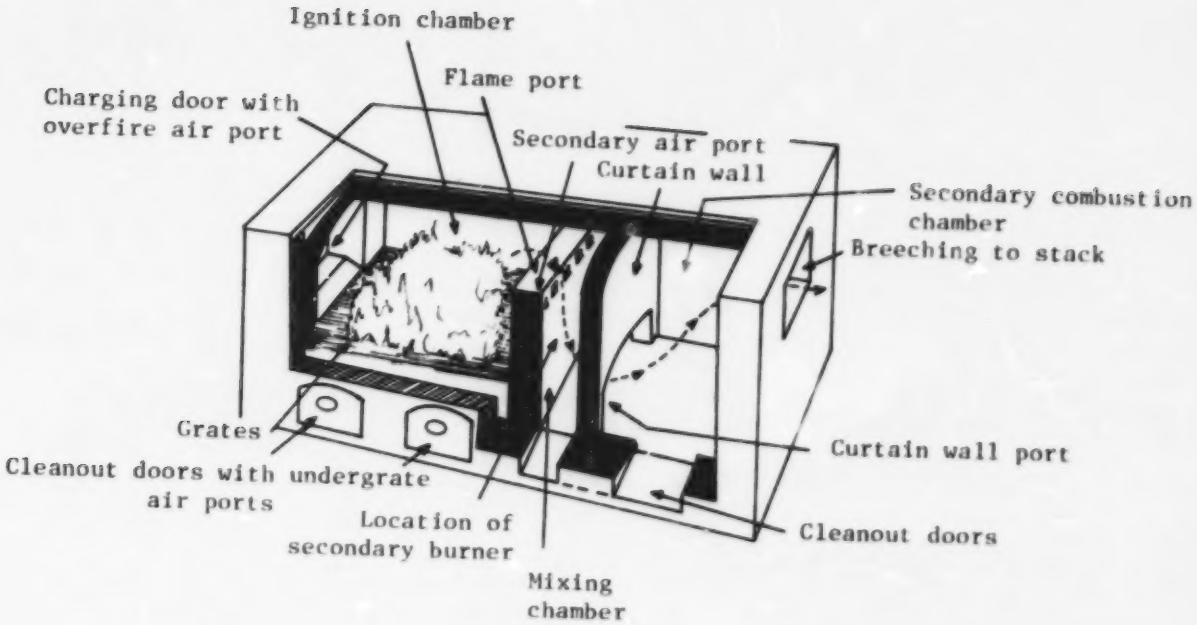


Fig. 3-16. Cutaway of in-line multiple-chamber incinerator

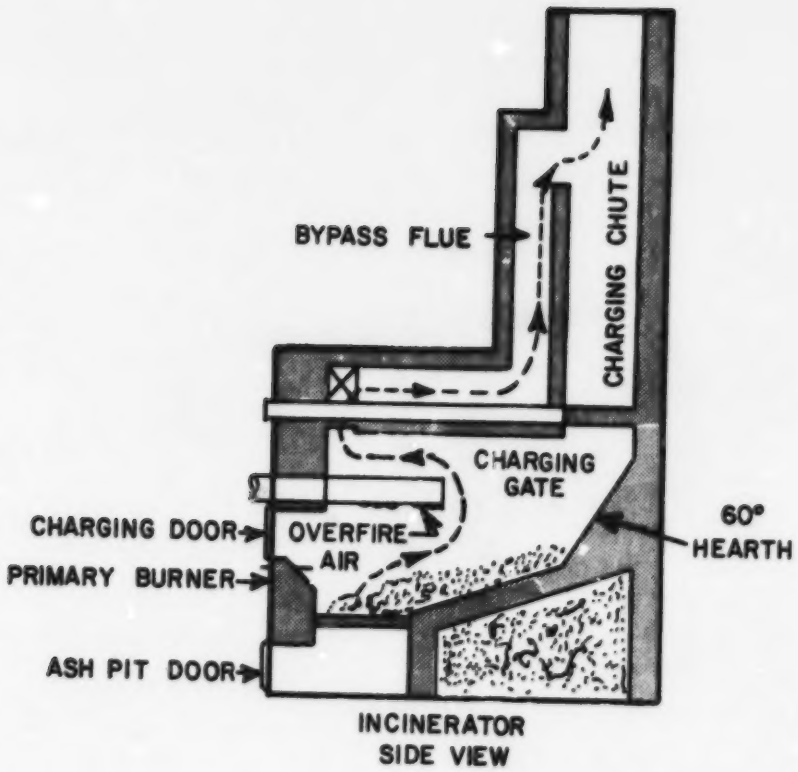


FIG. 3-17. Section of flue-fed incinerator.

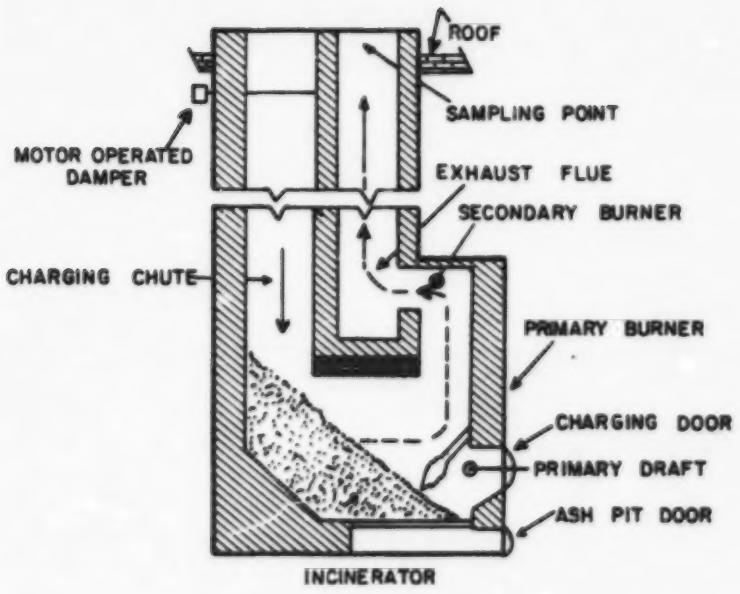


Fig. 3-18. Section of chute-fed apartment incinerator

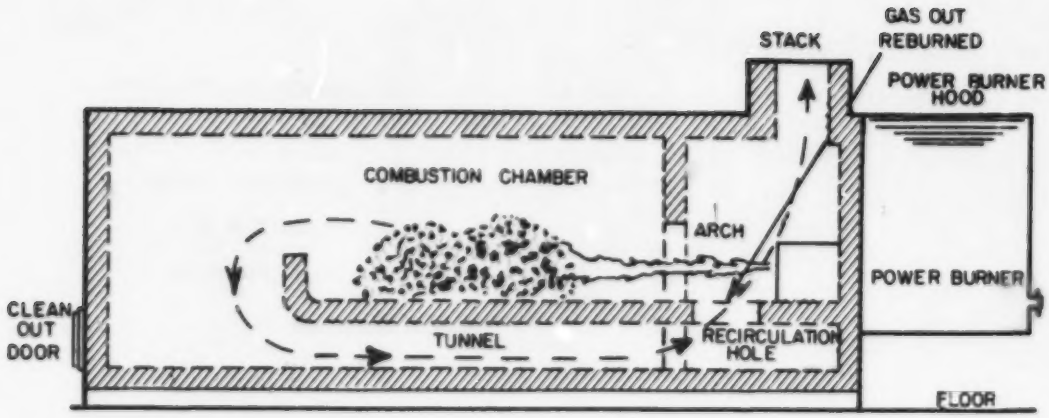


FIG. 3-19. Section of pathological incinerator

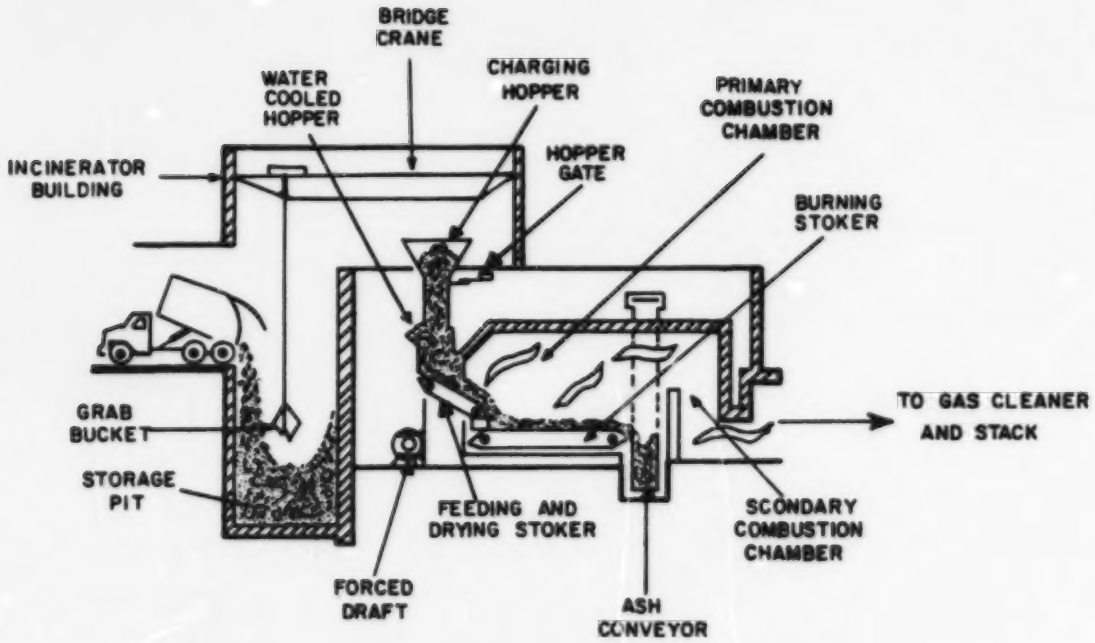


Fig. 3-20. Section of municipal incinerator

Incineration and open burning are used to reduce the weight and volume of solid waste. High-temperature incineration with excess air reduces emissions of particulates, CO, and smog-forming compounds such as aldehydes, hydrocarbons, and organic acids (which typify open burning), but increases nitrogen oxides emissions. Estimated CO emissions from incineration and other burning are shown in Tables 3-16 and 3-17.

Table 3-16. - ESTIMATED U.S. EMISSIONS IN 1968 FROM INCINERATION AND OTHER BURNING[1]

Category	Quantity Gkg/yr	CO emissions Mkg/yr
Municipal incineration	18	320
On-site incineration	41	410
Landfills	22.6	0
Open dumps:		
Burned	63.5	2 700
Unburned	118	0
Conical burners	27	1 760
On-site burned	32	1 350
Other unburned	4.5	0
Total		6 540

Table 3-17. - WASTE IN THE BRD (1970)[77]

Category	Quantity Gkg
Household	16
Commercial	4
Industrial	2
Building refuse	5
Mining and steel	20
Sewage sludge	18
Wrecked automobiles	1
Agricultural waste	190
Total	260

3.4 REFERENCES

1. OAP Data File of Nationwide Emissions 1970. National Air Data Center, Applied Technology Center, July 1972.

2. Statistical Abstract of the United States: 1970. 91st Edition, U.S. Bureau of the Census, Washington, D.C., 1970.

3. Jahrbuch f. Bergbau. Energie Mineralöl und Chemie, 1971.

4. Preliminary National Power Survey Estimates. Federal Power Commission. December 1969.

5. Statistik 1970, Vereinigung Deutscher Elektrizitätswerke, Ffm.

6. Dunphy, B. 1966 Oilheating Sales Analysis. Installations up 2.5% to 558,965. Fueloil & oil Heat. 26:29-35, January 1967.

7. F. Baum, Staub-Reinhalt. d. Luft 32 (1972) Nr. 2, S.54.

8. H. Schade, Schriftenreihe der LIB, Heft 26/1972 (UWD 30/72, S.6)

9. Emissions Kataster, Land Nord-Rhein-Westfallen.

10. Greaves, M. J., and A. English. Engineering Contributions to New Techniques of Iron Ore Agglomeration. In: Agglomeration, Knepper, W. A. (ed.), New York, Interscience Publishers, 1962. p. 419-453.

11. VDI Richtlinien, VDI 2095.

12. "Stat. Bundesamt, Düsseldorf-Eisen und Stahl."

13. McGannon, H. E. The Making, Shaping and Treating of Steel. 8th ed. Pittsburgh, U.S. Steel Company, 1964.

14. Schueneman, J. J., M. D. High, and W. E. Bye. Air Pollution Aspects of the Iron and Steel Industry. U.S. DHEW, PHS, Division of Air Pollution. Washington, D.C. PHS Publication No. 999-AP-1. June 1963.

15. VDI 2099.

16. Stat. Jahrbuch, Eisen und Stahl, 1971, S.10.

17. Eisen und Stahl, 4. Vierteljahresheft 1971, S.45.

18. Jackson, A. Oxygen Steelmaking for Steelmakers. London, George Newnes Ltd., 1964. 258 p.

19. A Systems Analysis Study of the Integrated Iron and Steel Industry. Battelle Memorial Institute. May 1969. Clearing House for Scientific and Technical Information. Accession No. PB 184576, PB 184577. Springfield, Va.

20. VDI Richtlinien, VDI 2112 (1966).

21. Staub Reinhaltung d. Luft 32 (1972, S.53.

22. Air Pollution Engineering Manual, Danielson, J. A. (ed.). U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. PHS Publication No. 999-AP-40. 1967.

23. D. Eickel pasch, Staub-Reinhalt. Luft 32 (1972), 52.

24. Minerals Yearbook 1967, Vol. I-II. U.S. Dept. of Interior, Bureau of Mines. Washington, D.C. 1968.

25. Electric Furnace Steelmaking, Vol. II. Theory and Fundamentals, Sims, C. E. (ed.). New York, Interscience Publishers, 1963.

26. DeCarlo, J. A., T. W. Hunter, and M. M. Otero. Coke and Coal Chemicals. In: Minerals Yearbook 1961. U.S. Dept of Interior, Bureau of Mines. Washington, D.C. 1962.

27. Eisen u. Stahl, 4. Vierteljahresheft 1971.

28. Powell, A. R. Gas from Coal Carbonization--Preparation and Properties. In: Chemistry of Coal Utilization, Lowry, H. H. (ed.). Vol. II. New York, John Wiley & Sons, 1945. p. 921-946.

29. H. W. Thoenes, Staub-Reinhalt. Luft 32 (1971), S.50.

30. Ozolins, G., and R. Smith. A Rapid Survey Technique for Estimating Community Air Pollution Emissions. U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. PHS Publication No. 999-AP-29. 1967.

31. Jahresbericht 71, MWV/AEV.

32. VDI Richtlinien, VDI 2440.

33. Petroleum Processing Handbook, Bland, W. F., and R. L. Davidson (eds.). New York, McGraw-Hill Book Co.

34. OAP Data File of Nationwide Emissions 1970. National Air Data Center, Applied Technology Center, July 1972.

35. Saxton, A. L., H. N. Weinberg, and R. O. Wright. Get Cheaper Coking Now with this New Design. Petrol. Refiner. 39:157-160, May 1960.

36. Zu Drucksache VI/2710 des deutschen Bundestages; Materlialien band zum Umweltprogramm der Dundes-regierung; Bonn 1971.

37. Noyes, R. Ammonia and Synthesis Gas 1967. Park Ridge, Noyes Development Corp., 1967.

38. Synthesis Gas--Shell Development Co. Hydrocarbon Processing. 46: 227, November 1967.

39. Elsbree, John J. Organic Chemicals. Chemical Engineering News. 46(37), September 2, 1968.

40. Statistiches Bundesamt IV C 63, Industrielle Produktion im Bundesgebiet, Chemische Erzeugnisse.

41. 25th Inventory of New Processes and Technology. Chem. Eng. 75(15): 104, July 15, 1968.

42. Oil Paint and Drug Reporter, May 4, 1964.

43. Winnacker-Küchler, Bd. 1, S.659.

44. Egalon, R., R. Vanhille, and M. Willemyns. Purification of Carbon Monoxide by Cuprammonium Carbonate Solutions. Removal of Carbon Monoxide by Cuprammonium Carbonate Solutions. Ind. Eng. Chem. 47: 887-889, May 1955.

45. Sittig, M. Organic Chemical Process Encyclopedia 1967. Park Ridge, Noyes Development Corp., 1967.

46. Synthesis Gas--Shell Development Co. Hydrocarbon Processing. 46: 227, November 1967.

47. Friedman, B. S., and S. M. Cotton. Production of Acids and Esters. Sinclair Refining Co., U.S. Patent No. 3,005,846. Official Gazette. U.S. Patent Office. 771(4):1081, October 1961.

48. Kurhajec, G. A., D. L. Johnston, and K. E. Furman. Production of Carboxylic Acids (Shell Oil Co., U.S. Patent No. 3,047,622). Official Gazette U.S. Patent Office. 780(5):1731, July 1962.

49. Natta, G., and P. Pino. Preparation of Succinic Acids (Lonza Electric and Chemical Works, Ltd. U.S. Patent No. 2,851,486). Official Gazette U.S. Patent Office. 734(2):484, September 1958.

50. Hagemeyer, H. J., Jr., and D. C. Hull. Process of Producing Oxygenated Organic Compounds (Eastman Kodak Co., U.S. Patent No. 2,784,167). Official Gazette U.S. Patent Office. 706(5):1221, May 1956.

51. Jaros, S., and C. Roming, Jr. Production of Aldehydes and Alcohols. Esso Research and Engineering Co., U.S. Patent No. 3,119,876). Official Gazette U.S. Patent Office. 798(4):993, January 1964.

52. Seefen, H. T., and W. R. Trutna. Low Pressure Production Formamides. (E. I. DuPont de Nemours and Co., U.S. Patent No. 2,866,822). Official Gazette U.S. Patent Office. 737(5):1265, December 1958.

53. Staib, J. H., W. R. F. Guyer, and O. C. Slollerbeck. Ketone Synthesis. (Esso Research and Engineering Co., U.S. Patent No. 2,864,864). Official Gazette U.S. Patent Office. 737(3):719, December 1958.

54. Private Communication with J. L. Parsons. E. I. Du Pont de Nemours and Co. November 11, 1968.

55. Friedman, R., and J. A. Cyphers. On the Burning Rate of Carbon Monoxide. J. Chem. Phys. 25(3):448-457, September 1965.

56. Singer, J. M., et al. Flame Characteristics Causing Air Pollution: Production of Oxides of Nitrogen and Carbon Monoxide. Bureau of Mines. Washington, D. C. Report of Investigations Number 6958. 1967. 34 p.

57. Mencher, S. K. Minimizing Waste in the Petrochemical Industry. Chem. Eng. Progr. 63:80-88, October 1967.

58. Horton, K. G. Carbon Black: Review and Forecast. Rubber World, 154(6):75-76. September 1966.

59. Harper, W. B. Carbon Black. In: Minerals Yearbook 1967. U. S. Dept. of Interior. Washington, D. C. 1967. p. 263-272.

60. Market Newsletter. Chem. Week. 103(21):41-42, November 23, 1968.

61. Del Gatto, J. V. Cabot Carbon Black Plant Goes Commercial. Rubber World. 158(5):56, August 1968.

62. Statistisches-Bundesamt IV C 63, Industrielle Produktion im Bundesgebiet, Chemische Erzeugnisse.

63. VDI 2580.

64. Drogin, I. Carbon Black. J. Air Pollution Control Assoc. 18(4): 216-228. April 1968.

65. Britt, K. W. Handbook of Pulp and Paper Technology. New York, Reinhold Publishing Corp., 1964. 537 p.

66. A Study of Air Pollution in the Interstate Region of Lewiston, Idaho and Clarkston, Washington. Division of Air Pollution. Cincinnati, Ohio. PHS Publication No. 999-AP-8. December 1964.

67. Control Techniques for Sulfur Oxide Air Pollutants. U.S. DHEW, PHS, CPEHS, National Air Pollution Control Administration. Washington, D. C. AP-52. January 1969. 85 p.

68. Letter. N. Plaks to J. McGinnity, Division of Abatement, NAPCA. Subject: Control Techniques for Carbon Monoxide Emissions. December 9, 1969.

69. Thoen, G. N., et al. The Effect of Combustion Variables on the Release of Odorous Sulfur Compounds from a Kraft Recovery Unit. TAPPI 51:329-333. August 1968.

70. Statistisches Bundesamt IV C 63, Industrielle Produktion im Bundesgebiet, Chemische Erzeugnisse.

71. Burt, R. B., and J. C. Barber. Production of Elemental Phosphorus by the Electric Furnace Method. Tennessee Valley Authority. Knoxville, Tenn. TVA Chemical Engineering Report No. 3. 1952.

72. Winnacker-Küchler, Bd. 2.

73. Incineration. In: Air Pollution Engineering Manual, Danielson, J. A. (ed.). U.S. DHEW, PHS, National Center for Air Pollution Control. Cincinnati, Ohio. PHS Publication No. 999-AP-40. 1967. p. 413-503.

74. De Marco, Jack, et al. Incinerator Guidelines--1969. U.S. DHEW, PHS, CPEHS, Environmental Control Administration, Cincinnati, Ohio. SW--13TS. 176 p.

75. Black, R. J., et al. The National Solids Wastes Survey. Presented at 1968 Annual Meeting of the Institute for Solid Wastes of the Americal Public Works Association. Miami Beach, Fla. Oct. 1968.

76. National Air Pollution Control Administration, Reference Book of Nationwide Emissions. U.S. DHEW, PHS, CPEHS, NAPCA. Durham, N.C.

77. Zu Drucksache VI/2710 des deutchen Bundestages; Materialienband zum Umweltprogramm der Bundesregierung; Bonn 1971.

4. CONTROL TECHNIQUES

Techniques for controlling emissions of CO from stationary fuel combustion sources include source shutdown, energy substitution, energy conservation, good operating practice, and mechanical systems of various types. Source relocation and tall stacks may be used to aid in the dispersion of CO. The mechanical devices for controlling emissions from stationary process sources are by far the most important and thus comprise the major subjects of this section.

4.1 SOURCE RELOCATION OR SHUTDOWN

Source relocation will eliminate CO emissions from the original source location but will transfer all air pollution effects to another area. Ordinarily, source relocation is considered when a new plant is to be built to replace one that has created air pollution problems. In one process, the channel process for manufacturing the colorant in ink black, source relocation is the only feasible control technique. The process requires a natural draft through the hot house, and any attempt to confine the emissions from these hot houses disturbs the natural draft and reduces the yield and quality of the black; therefore, the only control is to move the plant if the emissions (probably particulates before CO) get too high.

Source shutdown is a drastic control technique, but it should not be completely disregarded if CO levels threaten the public health in emergency episodes or if lawful orders to abate are ignored.

4.2 ENERGY SUBSTITUTION OR CONSERVATION

Energy substitution involves replacing an undesirable fossil fuel with one that generates less pollution. Substitution of gas- or oil-fired units for coal-burning grate- or stoker-type units will reduce CO emissions.

Hydroelectric power is too limited in growth potential in the United States to be considered as a substitute for fossil-fuel energy. Even nuclear power generation will not entirely eliminate CO emissions because of the need for standby fossil-fuel power-generating facilities.

It is sometimes difficult to predict the effects of energy substitution, since among energy sources heat requirements differ for seemingly identical applications; for example, heat requirements for space heating by electricity or by fossil fuel will differ since buildings that are heated electrically are normally better insulated than buildings heated with fossil fuel.

Discussion of fuel substitution is probably academic for large, well-operated units (e.g., power plants with low emission rates); however, conversion from coal to oil or gas will reduce emissions from homes and numerous other small users concentrated in limited areas. Thus, energy substitution can be effective; it has special value for control of low capacity sources for which the cost of gas-cleaning equipment would be excessive. Table 4-1 gives estimated emission factors for small heat-release rate units (2.92 MJ/s);[1] for coal, the relative emission rate decreases with increasing size of combustion unit.

Energy conservation reduces CO emissions by reducing fuel consumption. For steam electric power generating plants, Table 4-2 shows U.S. trends in efficiency improvements--primarily, the use of higher temperatures and pressures; corresponding data for the BRD are shown in Table 4-3. Typical heat contents of fuels used in the BRD are shown in Table 4-4. Newer developments--the magnetohydrodynamic, the electrogasdynamic, and the fuel cell--have promise of improving efficiency even more than the current improvements.

Table 4-1. ESTIMATED CARBON MONOXIDE EMISSION RATES FROM FOSSIL FUELS AT DUTY OF 2.92 MJ/s

(mg/s)

Fuel	CO
Coal	252
Oil	1.69
Natural Gas	0.04

Table 4-2. CONSUMPTION OF FUELS PER KILOWATT-HOUR BY ELECTRIC UTILITIES[2]

Year*	Coal (kg)	Oil 10^{-3} m^3	Gas m^3
1955	0.431	0.322	0.342
1960	0.399	0.296	0.308
1965	0.389	0.284	0.297
1968	0.395	0.288	0.292
1969 (prel.)	0.399	0.292	0.294

*Prior to 1965, excludes Alaska and Hawaii. Includes use of fuels for standby purposes.

Table 4-3. SPECIFIC CONSUMPTION BY ELECTRIC UTILITIES IN THE BRD[3]

Actual consumption				Projected consumption	
Year	GJ/kg-kw-hr	Year	GJ/kg-kw-hr	Year	GJ/kg-kw-hr
1950	21.7	1961	12.5	1971	10.5
1951	19.1	1962	12.3	1972	10.3
1952	17.8	1963	12.0	1973	10.2
1953	16.9	1964	11.7	1974	10.1
1954	16.2	1965	11.5	1975	10.1
1955	15.4	1966	11.2	1976	9.9
1956	14.9	1967	10.9	1977	9.9
1957	14.4	1968	10.8	1978	9.9
1958	13.8	1969	10.7	1979	9.8
1959	13.3	1970	10.7	1980	9.8
1960	12.8				

Table 4-4. HEAT CONTENT OF FUELS USED IN THE BRD[4]

Fuel	GJ/kg-kw-hr
Brown coal	11.5
Hard coal	10.7
Oil	9.1
Gas	9.1

4.3 GOOD PRACTICE

Good practice includes proper selection, installation, operation and maintenance of combustion operations to minimize CO emissions. Guidelines are published by fuel industries, equipment manufacturers, engineering associations, and government agencies; help on individual problems should be solicited from these sources.

Selection of components of the combustion system--the fuel-handling system, the draft system, the fuel-burning system, the flues and stacks, the ash-handling system, and the combustion controls--must be made to ensure operation within design limits and to prevent excessive oxygen in the flue gas and excessive emissions of CO. Therefore, the load must be accurately estimated, the design capacity of the system must be sufficient to carry the maximum load, and future increases in load requirements must be considered. The minimum design capacity of one unit of the combustion system must carry the minimum load requirements, and the total combustion system must carry any load between maximum and minimum. Careful attention to these matters can avoid overloading--firing in excess of the design rate--which is perhaps the greatest cause of excess CO emissions from a combustion unit. Furnace design (Table 4-5) and boiler-firing method (Table 4-6) affect the quantity of CO emissions. Thus, proper application of basic engineering principles to furnace design can lower overall fuel requirements and substantially lessen the likelihood of ambient air pollution by CO.

The selection of the flue system is especially important, since the flue delivers the products of combustion to the atmosphere and simultaneously maintains furnace pressure and combustion rate. (In some furnaces, a positive pressure exists; in others, a zero or slightly negative pressure.) If the flue is too small, it impedes the flow of escaping gases and combustion

Table 4-5. CARBON MONOXIDE EMISSIONS FROM GRATE-FIRED COAL-BURNING UNITS[5]

Type of unit	Unit size (MJ/s)	CO emissions (μg/J)
Chain grate	43.1	0.22
Spreader stoker	17.3	<0.04
Underfeed stoker	1.2	0.07
Underfeed stoker	0.88	0.06
Underfeed stoker	0.019	0.47
Hand-fired stoker	0.033	1.51

Table 4-6. CARBON MONOXIDE EMISSIONS FROM SUSPENSION COAL-FIRED BOILER UNITS[5]

(ng/J)

Type of firing	CO emissions
Vertical	7.3
Corner	4.7
Front wall	2.2
Spreader stoker	12.5
Horizontally opposed	18.8

products, it causes a back pressure, hinders the flow of air to the combustion chamber, reduces the quantity of fuel that can be burned efficiently, decreases temperature (may extinguish the flame) and the burning rate, and thus causes CO formation. If the flue is too large, the products of combustion leave too fast under fixed chimney draft, the furnace pressure decreases, and excess air infiltrates the chamber; consequent fuel waste, temperature variation and heat distribution, and possible ignition failure increase CO emissions from coal or oil. Some conditions (e.g., high flame temperature) favor complete fuel combustion but tend to promote formation of nitrogen oxides.

Installation of equipment should be done only by qualified personnel. Care must be taken to ensure following the manufacturer's plans and instructions.

Operation is usually in accordance with several general principles; CO emissions are minimized by (1) high combustion temperatures but low effluent temperature; (2) intimate contact of fuel, oxygen, and combustion gases; and (3) rapid reaction rate and sufficient residence time. Good practice requires that these principles be followed.

Periodic inspections and use of sensitive monitoring systems should be utilized as indicators of needed repair. Both proper installation and maintenance are essential for clean, efficient operation and reduction of CO emissions.

4.4 AUTOMATIC BURNER CONTROL SYSTEMS

Variations in load of combustion systems may not elicit sufficiently rapid response from operators in manually operated systems; thus, automatic control of the fuel-air ratio generally offers greater efficiency, lower CO

emissions, and lower operating costs than a manual control. The greater the load variation (or the more complex and the larger the installation), the easier it is to justify the selection of complex, comprehensive controls that limit fuel consumption, that follow load demands without lags, that increase safety, and that reduce ambient air pollution.

Exclusive of the selection and efficient use of fuel, the most important factor to consider for CO abatement in stationary fuel combustion sources is the selection of the type of control system. Control systems are of three general types.

1. The on-off control system is the simplest but the least effective for maintaining a well-balanced fuel-air ratio. A pressure signal from a steam header or a boiler drum regulates the fuel-air flow; that is, steam variations between set limits signal the burners to either light or shut down. Because the boiler is constantly being heated or cooled, an even temperature is not maintained, complete combustion of the fuel is achieved during only part of the cycle, and the amounts of excess air and CO emissions are high. This type of simple control is used on small fire-tube boilers, heaters, etc., to minimize investment.
2. The position-control system can maintain an acceptable fuel-air ratio over the operating range of slightly fluctuating loads. Like on-off control, boiler pressure variations in this system signal the need to reposition dampers and valves to adjust air-fuel supply to demand. This type of control is most common on package and medium-sized boilers.
3. The metering system, the most elaborate control, maintains the best continuous fuel-air ratio over the operating range because

it anticipates load. It measures steam flow and pressure, fuel flow, and air flow; it compares steam requirements with feed-water input to determine the correct firing rate; and it responds rapidly due to its feedback control system. This system is used almost exclusively on utility boilers.

Although the on-off system is simplest of the three types, it offers the least amount of control over the fuel-air ratio; more complicated, the position-control system varies the ratio over a range of loads for a more efficient firing rate; the metering system, which is the most sensitive to load variation, controls the ratio over constant and flucutating loads.

4.5 AFTERBURNERS

Afterburners for CO control are most often used on iron cupolas, which without effluent control systems, emit CO, dust, and fumes directly to the atmosphere. Cupolas with efficient particulate-collecting systems have afterburners for burning particulates (e.g., coke breeze and smoke and oil vapors) from the oily scrap in the charge and for burning CO to avoid handling explosive gas mixtures.

While an afterburner may be installed as a separate unit, the common practice is to use the upper portion of the cupola above the charging door as the afterburner. When this is done, the height of the conventional cupola must be increased to provide adequate retention time to complete the combustion of the afterburner.

The balanced-blast cupola differs from the conventional cupola; it has three or more rows of tuyeres to admit air at several levels, instead of at only one or two levels, and it is fed preheated blast air instead of cold ambient air.[6] Adjusting individual tuyeres maximizes CO in the bottom of

the cupola and minimizes CO in the top preheat zone. Preheating airfeed to about 810 K before admitting it to the tuyeres increases heat input to the cupola, decreases the amount of coke required for melting, decreases the amount of combustion products, and tends to decrease CO emissions in the exit gas from the preheat zone. Uniform melting and reduction in bridging can be obtained, and freezing near a tuyere can be prevented by temporary shutoff of air at that tuyere; these factors also decrease coke consumption and CO emissions.

An afterburner should be designed to raise the temperature of the combustibles, inspirated air, and cupola gases to at least 920 K.[7] It should also create enough turbulence in the gas stream for thorough mixing of combustibles and air inspirated through the charging door to the preheat zone. The geometry of the combustion zone should provide a retention time of at least one-fourth second. One device proved successful in promoting mixing in large-diameter cupolas is the inverted cone (Fig. 4-1).[8]

Other necessary afterburner design features are:

1. A steady flame that is neither extinguished nor affected by the cupola charge and that relights automatically.
2. An automatic modulating system of the main burners that is controlled from a thermocouple in the stack and that cuts off the main burner flame, but not the pilot, if cupola gases have sufficient CO to affect the control temperature.
3. No interference with the cupola charging system or melting process.

These features are illustrated in Figs. 4-2 and 4-3. A cupola control system employed in the BRD is shown in Fig. 4-4.

A recent application of afterburners is in the removal of carbon monoxide (CO) from the exhaust gases of the combustion of plastic wastes.

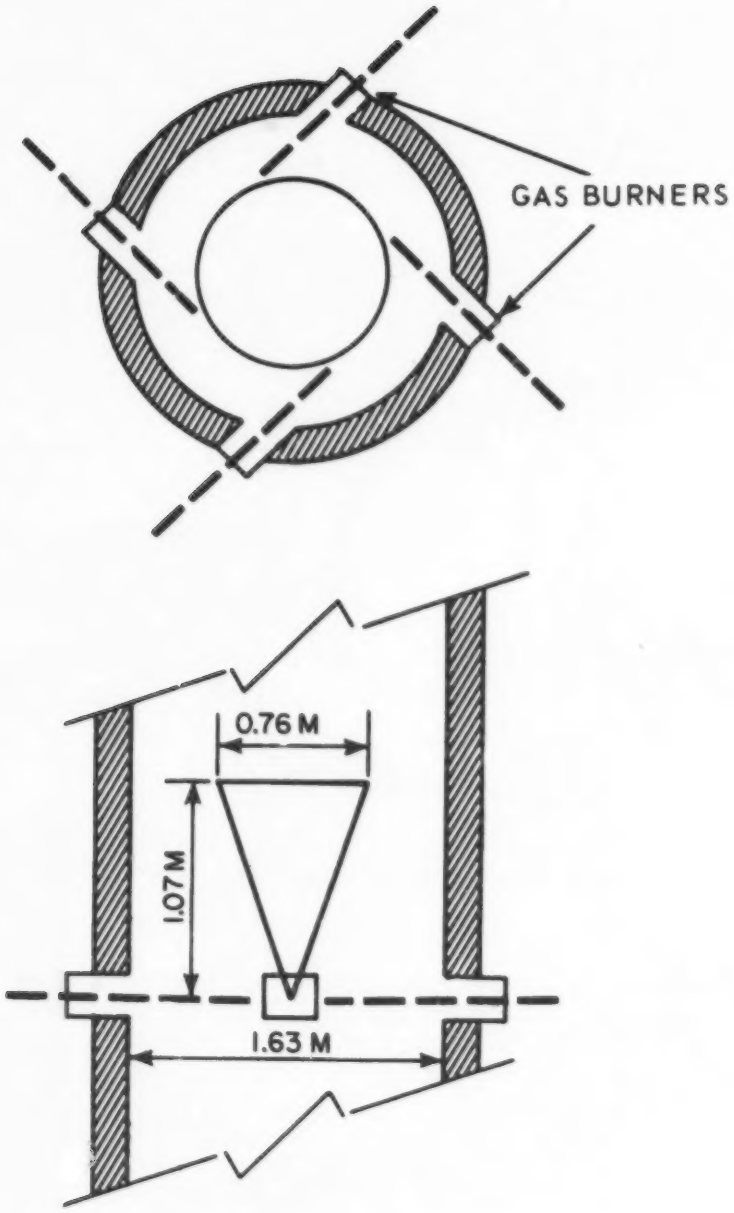


Figure 4.1 Integral afterburner with inverted cone installed in top part of cupola to create turbulence to ensure complete combustion

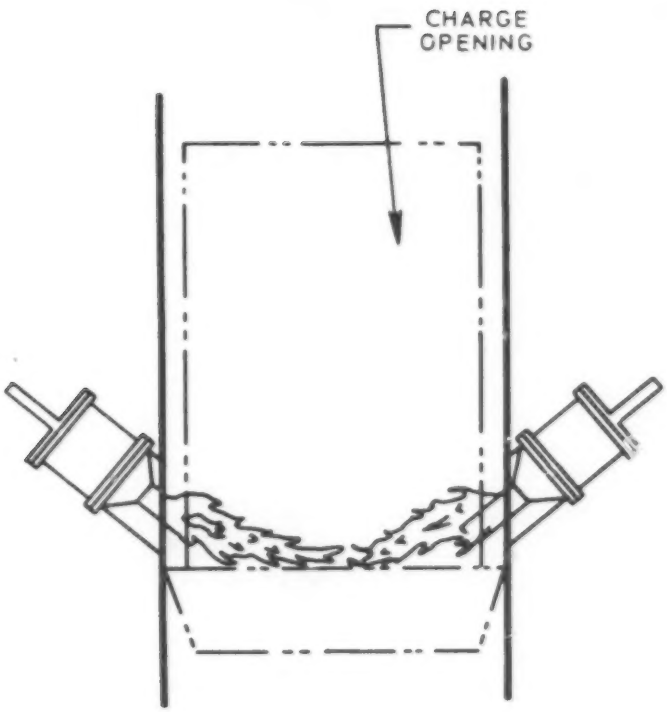


Fig. 4-2. Diagram of afterburner system showing flame introduced at most favorable location to ignite cupola gases.

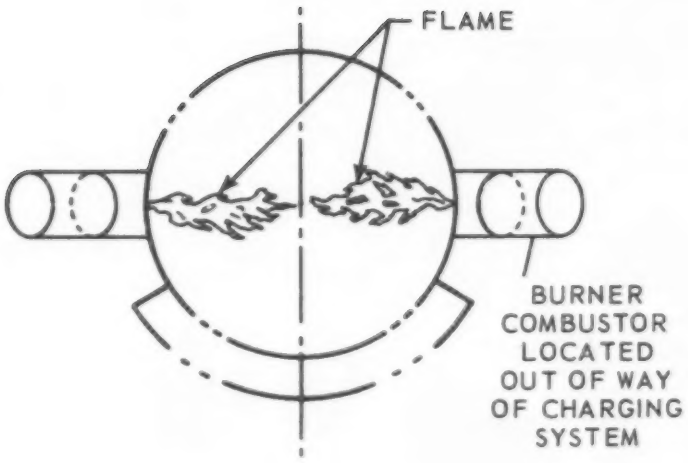
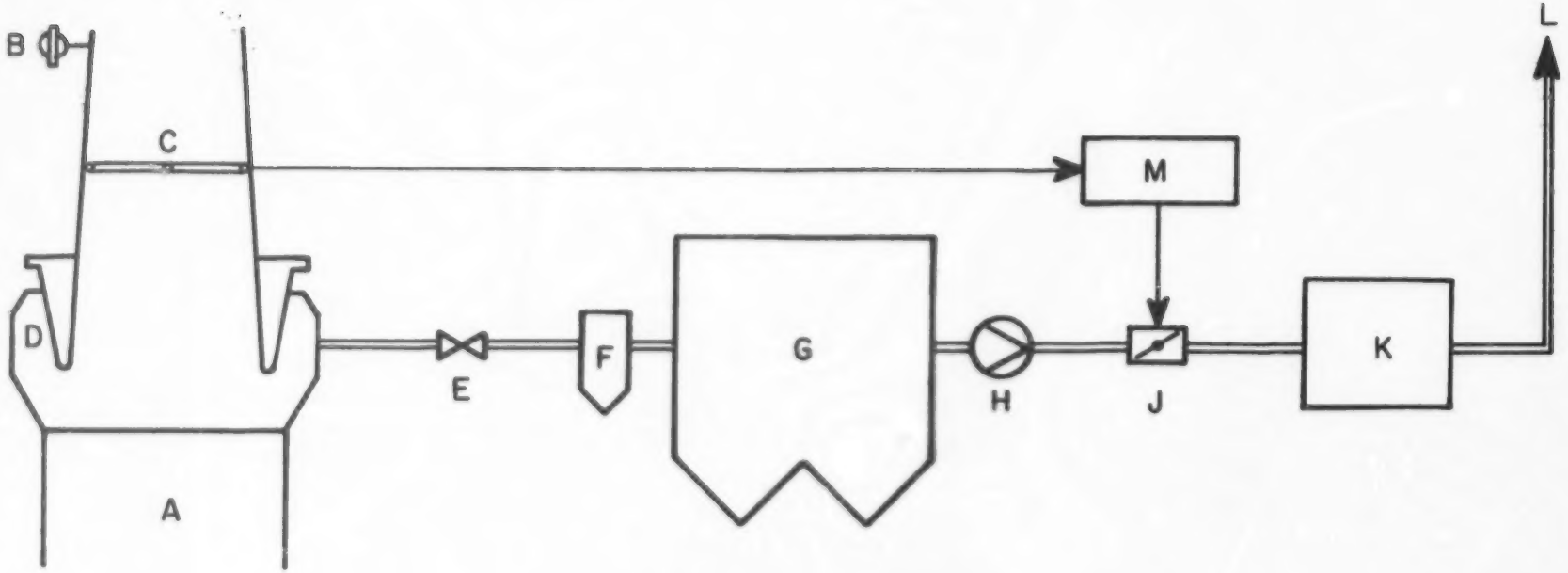


Fig. 4-3. Diagram of flame in afterburner system that is neither extinguished nor affected by cupola charge.



A Cupola furnace
B Level indicator
C Pressure probe
D Offgas manifold
E Gate valve
F Regulator
G Filter
H Ventilator
J Damper
K Collector
L Stack
M Control element

Fig. 4-4. Offgas dust recovery system

Incineration of such wastes produces other pollutants for which other control methods must be provided, but secondary combustion eliminates both carbon monoxide and soot.[9]

4.6 WASTE-HEAT BOILERS

The CO waste-heat boiler, most prevalent in the petroleum industry, uses the combustion heat of CO and the sensible heat of the regeneration gases from catalytic cracking to recover heating values. The CO and other combustibles (mainly hydrocarbons) are oxidized to carbon dioxide and water and are thereby eliminated as air pollutants.

Boilers do not have an oxidation catalyst chamber for conversion of CO to carbon dioxide. In most cases, supplementary fuel (fuel oil, refinery process gas, or natural gas) is required for a minimum CO gas-combustion temperature of 1 250 K for stable operation within the primary furnace section.[10]

The CO boiler may be vertical with either a rectangular or a circular cross-section of water-cooled walls (Fig. 4-5). The outer dimensions of a typical rectangular boiler are 9.75 m wide, 13.4 m deep, and 19.5 m high, with a 60.9 m high stack.[11] The boiler is equipped with a forced-draft fan and four sets of fixed, tangential-type burners (one set for each corner). A typical set of burners includes two CO compartments, four fuel gas nozzles, and two steam-atomized oil burners (Fig. 4-6). The burners, approximately 0.46 m wide by 1.83 m high, are arranged slightly off-center to achieve tangential-type mixing of the gases for more nearly complete combustion.

Regeneration gases from the fluid catalytic cracking (FCC) unit are normally delivered to the inlet of the CO boiler ductwork at about 860 K and 13.7 kN/m^2 (gauge). Whenever the regenerator gases first pass through an

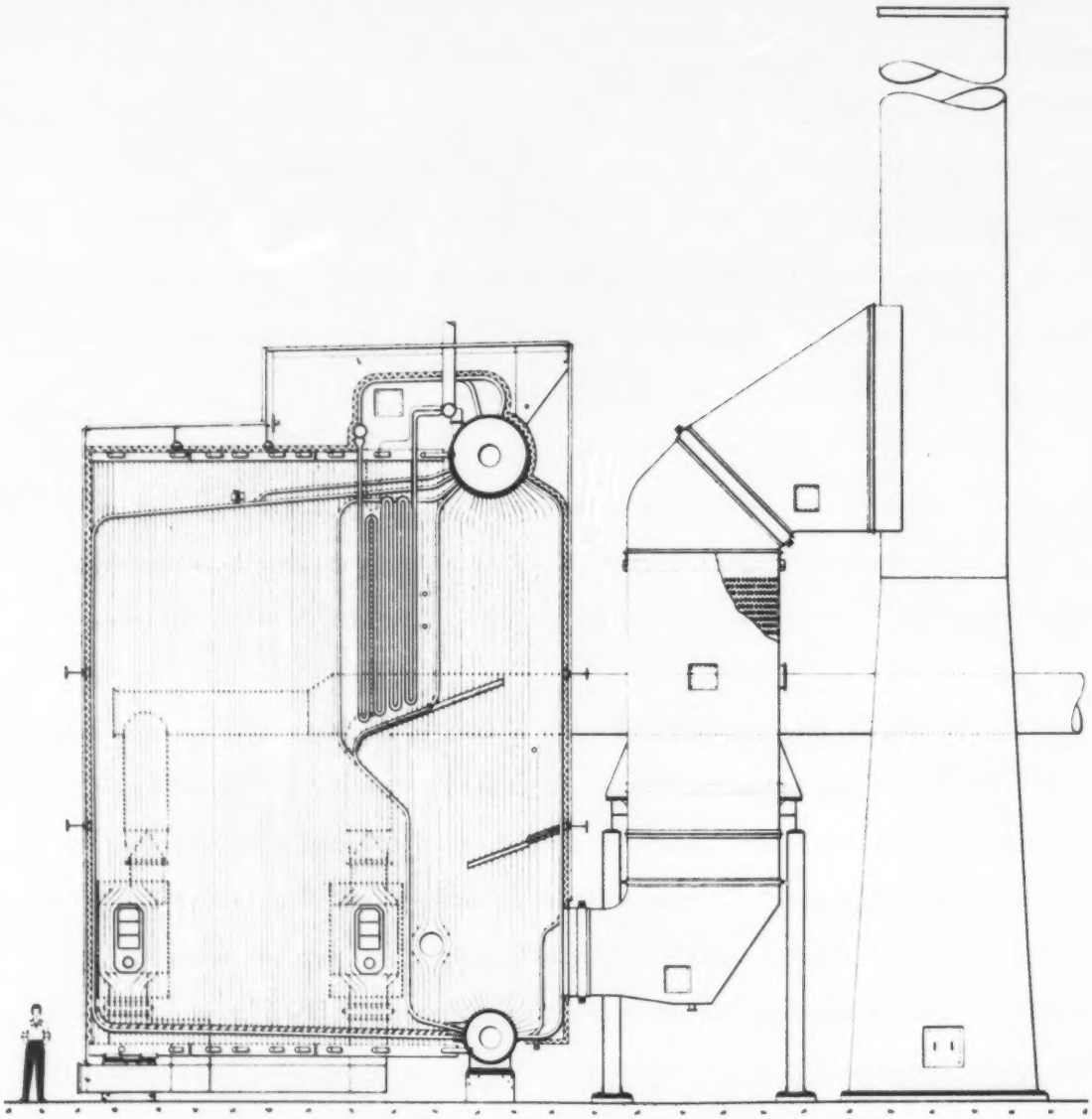


Fig. 4-5. Water-cooled carbon monoxide waste-heat boiler.

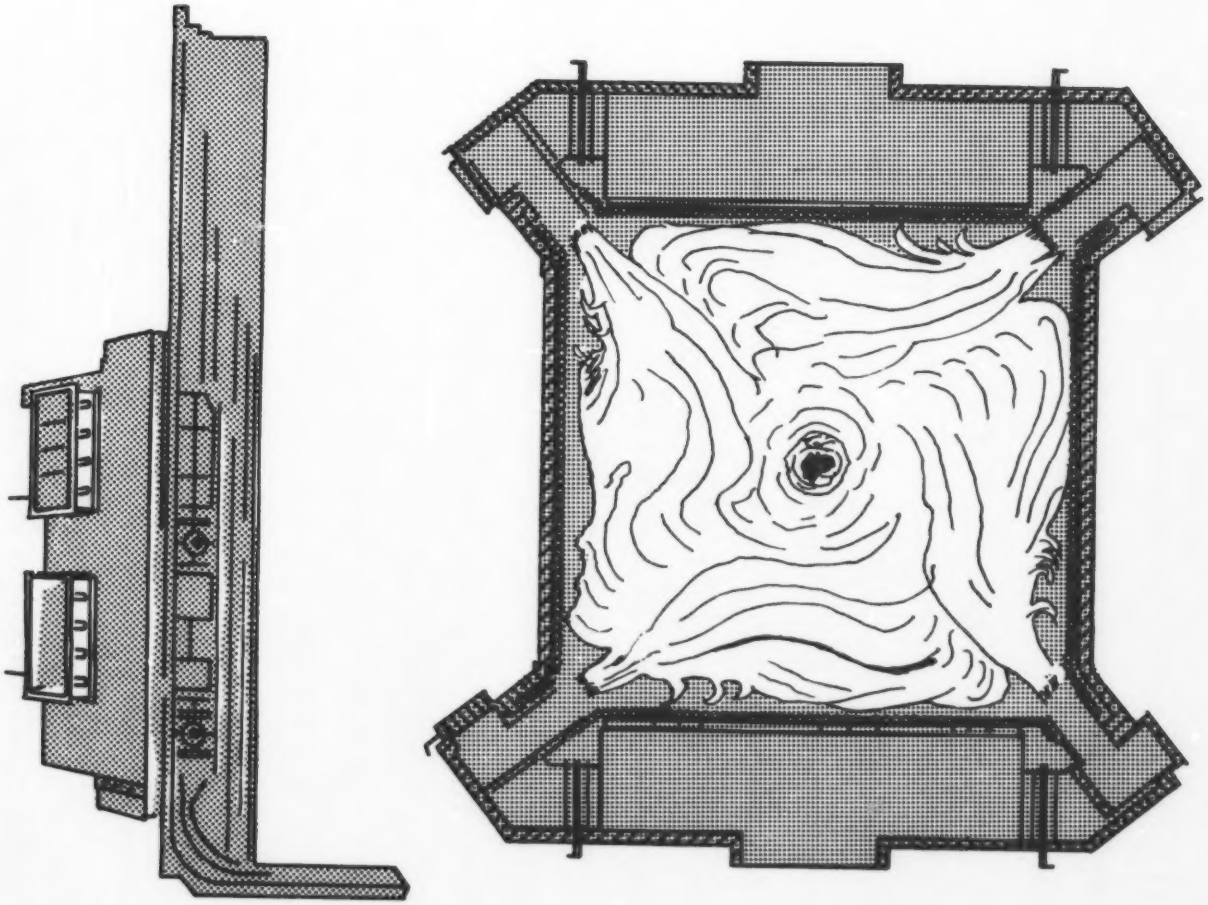


Figure 4-6. Corner-fired burners of a carbon monoxide waste-heat boiler (left, elevation view showing a typical set of burners for one corner; (right) plan view of firebox showing location of the four sets of burners.

electrical precipitator, the inlet gas to the precipitator must be cooled below 530 K. The CO boiler receives regenerated flue gas at 500 K to 530 K. Additional heat must be supplied since to ignite the CO, the air-CO mixture must be at least 920 K.

After ignition, the CO must be fed at a gradually increasing rate through well-distributed ports into a stream of much hotter combustion gases (without any major chilling effect), for the temperature to be high enough in the combustion chamber to convert CO to CO_2 with minimum auxiliary fuel.

To consume completely the CO-bearing offgas during operating-load fluctuations, temperatures of 1 250 K are needed. However, efficient CO combustion and stable ignition with minimum auxiliary fuel can be achieved at 1 080 to 1 140 K in hot refractory combustors if the chamber design promotes thorough mixing of auxiliary fuel and gas and if the chamber size provides adequate residence time. In the ideal design, ignition is sustained by stored radiant heat energy in the refractory setting, rather than by direct mixing with hot gases generated by the auxiliary burners. Maximum contact between the hot refractory walls and the fuel gases greatly accelerates the rate of combustion and lessens the need for auxiliary burners. With sufficient hot refractory, the CO burns stably, even if the auxiliary burners are out of service. When a heat sink (particularly a relatively cold surface) contacts the combustion chamber, it greatly reduces combustion efficiency and thus increases CO emissions. Undesirable are low-heat-capacity settings typical of firebrick and combustion volumes that are surrounded by cold, heat-absorbing surfaces; desirable are refractory enclosures with maximum heat storage--these prevent loss of ignition and pulsating detonation.

4.7 MECHANICAL SEALING

Pressure vessels, heat exchangers, and pipelines are commonly protected against overpressure by code-specified safety (or relief) valves or rupture discs.[12,13] Individual vessels, heat exchangers, and even sections of piping that can be blocked off require safety valves.

The spring-loaded safety valve opens to relieve pressure in the system and then reseals itself. The disc, a thin metal diaphragm made of corrosion-resistant aluminum, platinum, or one of many alloys and installed between flanges, ruptures at a certain difference in pressure on the two sides. (normally, the outside pressure is atmospheric).

Because emissions would not only cause losses of raw material, either CO or hydrogen, but also constitute a toxic or fire hazard, the chemical industry adapted refinery and oil-processing knowhow to applying equipment to its own special needs. Results of the adaptations are continuous, automatically controlled process plants featuring seamless pipe and welded pressure vessels--made, assembled, and tested strictly according to codes.[14,15] The old code for piping (U.S.A. Standards Institute Code B 31.3 for Petroleum Refinery Piping) gives minimum standards for chemical construction firms and chemical engineering staffs; the new 1970 code (B 31.6 for Chemical Plant Piping[16,17]) includes provision for handling lethal fluids (e.g., HCN gas) and for piping items (e.g., glass) that are mechanically damageable. A long, complicated code (the American Society of Mechanical Engineers Code for Unfired Pressure Vessels, Section VIII) for many types of vessels including reactors, surge tanks, and separators is complied with by approximately 25 of the states; this code specifies many details of design and strength of materials as well as such details as pneumatic and hydrostatic tests,

inspection of welds, and qualification and testing of welders. Vessel failures are extremely rare when vessels are used as designed in accordance with this code. In the case of synthesis gas, the hydrogen (not the CO) is difficult to contain so the type of steel used to retain the hydrogen is specified for the expected process conditions.[18]

Each equipment piece or plant section to be protected must be carefully examined to determine what conditions can cause gas evolution, blockage, or overpressure: (1) chemical reaction out of control, (2) failure of cooling water, (3) bursting of an exchanger tube, (4) blocking off a vessel or line, and (5) fire. Fire, often the governing condition which generates the most vapor, is often the basis of design for the safety valve or rupture disc.

4.8 HOODS

High-velocity oxygen stream impinging on the surface of the molten iron in a basic oxygen furnace generates extreme heat and large amounts of iron oxide fumes. The fumes are collected by either an open or a closed hood; then, they are cleaned by high-energy scrubbers or electrostatic precipitators and stored until they are used either as fuel or as a raw material for chemical manufacturing.

A diagram of a system with a closed hood designed to minimize infiltrated air is shown in Fig. 4-7. Figure 4-8 illustrates an open-hood system: Gases generated at the furnace are burned with excess air and cooled below ignition temperature with water sprays in a water-jacketed hood and quench chamber; as the gas stream passes the spray header (acting as a baffle), large particles fall into the spark box and then to a settling tank; as the stream passes through the flue connecting the spray chamber to the gas inlet, the gas is further cooled, the gas flow decreases, and large particles drop into the expansion chamber before the gas enters a plant precipitator for final cleaning.

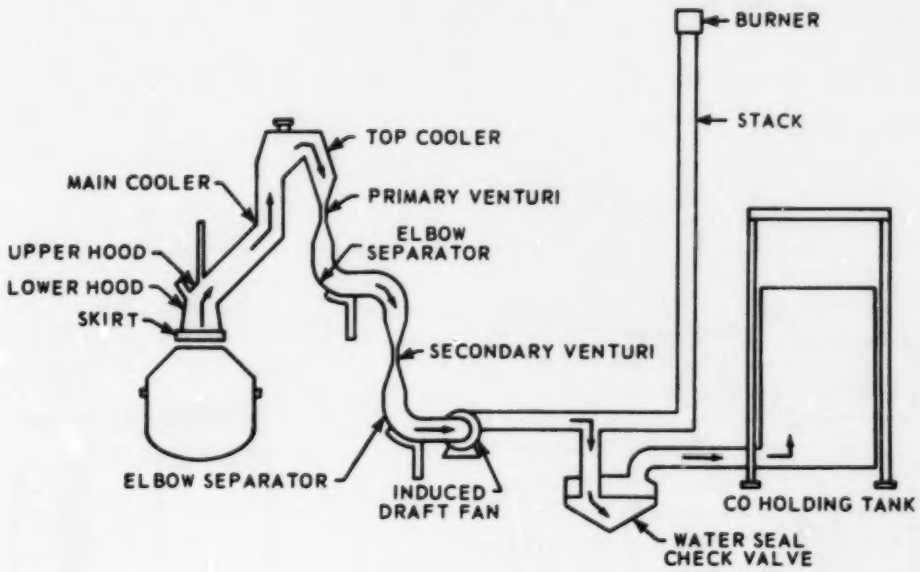


Fig. 4-7. Basic oxygen furnace with closed hood and gas-cleaning and storage system.

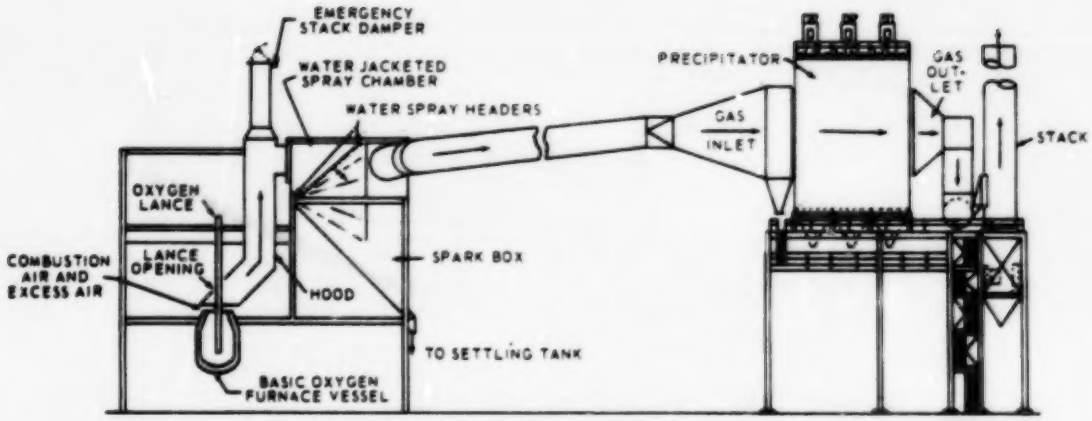


Fig. 4-8. Basic oxygen furnace with open hood and gas-cleaning system.

Hoods must be water-cooled because satisfactory refractory linings have not been developed.[19] Cold-water hoods of parallel wall-panel construction operate at low pressures and high flow rates, and the cold water prevents scale deposits. Hot-water hoods of a tubular design use high-pressure water and high water temperature differentials. Steam-generating hoods (Fig. 4-9) designed to take advantage of the latent heat of vaporization are constructed to tubular-membrane wall panels.[19]

For safety, the open hood usually admits more air than is needed to burn completely the CO in the hood; thus, the effluent volume is as much as 25 times the volume of the oxygen used, and the length of the hood should be sufficient to assure complete combustion of CO before the gas is cooled in the quench chamber.

A cold-water hood requires copious amounts of water, and if water is recirculated, the system requires large water-cooling towers. If not, cold-water hoods are usually lowest in capital cost. Both a hot-water and a steam hood require treated boiler feedwater. Hot water generated for the hoods may serve as sources for other uses or may be recirculated through a water-cooling tower or some type of heat exchanger. Steam is generated in cycles, and the demand for it does not coincide with the cycles; therefore, accumulators are required for storage and for recovery of saturated steam. If there is no demand for saturated steam, super-heaters and air-cooled condensors can be installed after the accumulators.

4.9 FLARES

After a vapor-collection system receives gas and liquid from the discharge side of safety valves and rupture discs, a knockout drum separates liquid from the gas stream; and a flare, commonly an elevated stack with a

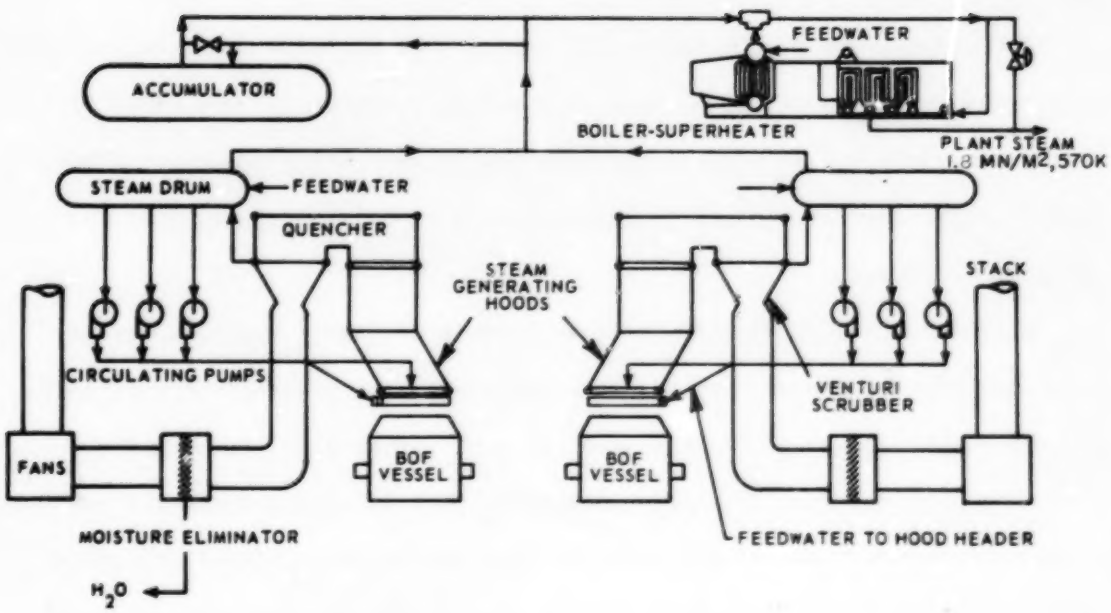


Figure 4.9. Open-hood system with steam-generating hoods

pilot burner, ignites the gas. A small bypass takes care of normal gas flows, and a water seal accommodates large emergency flows. Water seal pots have been used in reformer plants to limit pressure and to release sudden gas accumulations.

Figure 4-10 illustrates a vapor collection system and a flare used in a chemical plant or complex. The header collects blowdown and relief and discharges both into at least one separator drum,[20] from which waste liquid is pumped to disposal. The header may be purged with gas during startup before the flare is ignited by a pilot light. A flame arrestor (shown at the base of the flare stack) and an inert purge gas (e.g., nitrogen) guard against flame flashback.

If gas velocity of the flare is too high, the flame can be blown out. Blowout and consequent CO release are prevented by designing within certain stack velocities. (If blowout occurs, remote reignition is accomplished by the pilot burner.)

In designing the flare, safety is important.[21] Because a large flare may radiate enormous amounts of heat, it may have to be elevated from structures and personnel to 61 m or more. Safety can also be increased by purging at such a rate that the oxygen concentration 7.6 m from the top of the stack is less than 6 percent.[22] Purge gas composition depends on how the original synthesis gas was used. It may be high in CO. One manufacturer reports sending purge gas from the methanol synthesis to the reformers that make ammonia synthesis gas. It may be burned in a flare--a flame maintained out-of-doors at the end of a waste-gas-collection system to burn both regular miscellaneous vapor wastes and emergency vapor releases. However, purging is costly, and molecular seals[23] are commonly required to reduce purge-gas requirements and atmospheric emissions.

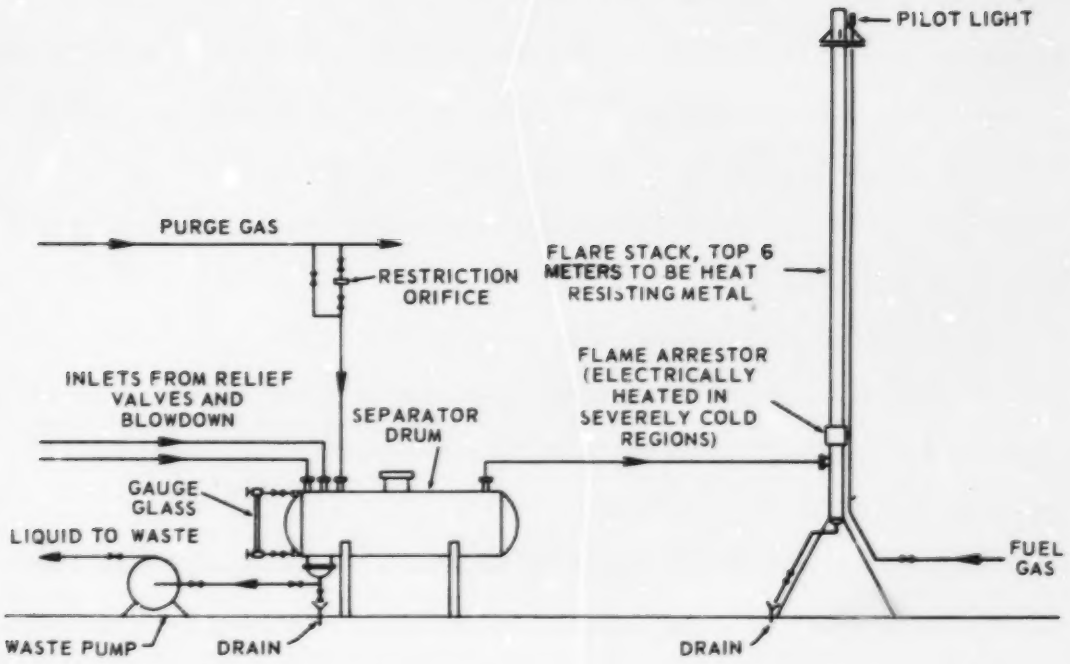


Figure 4.10. Blowdown and relief collection system

In the United Kingdom, two plants that manufacture furnace black use a flare on the stack to incinerate and control CO successfully.[24] Catalytic incineration is not practical for CO concentrations in the 5- to 10-percent range because the operating temperatures exceed 810 K, well above the range for catalysts.[25] The process for making furnace black may at some time have to be controlled in the United States.

Steam injection can frequently oxidize carbon monoxide to carbon dioxide when added to the feed gases to flares in petroleum refineries.[26]

4.10 MISCELLANEOUS CONTROL TECHNIQUES

4.10.1 Waste Disposal With or Without Incineration

For air pollution control, the most satisfactory techniques of solid waste disposal are those without incineration. Sanitary landfills are good techniques if land and fill material are available--that is, approximately 1 480 m^3/1 000 persons annually for waste production of 2.4 kg/day for each person,[27] and cover material approximating 20 percent, by volume, of the compacted waste. Another technique is to shred, bale, load, and ship refuse on rail cars to abandoned strip-mine landfill sites.[28] A third technique, composting, is being tested on a practical scale[29] for disposal of garbage. Dumping at sea, practiced by seacoast cities, has been forbidden by the U.S. Government because garbage floats back to shore; however, refuse that is ground and compressed into bales, wrapped in chicken wire, coated with asphalt, and dumped far out at sea reportedly remains intact at the ocean bottom. The practice of grinding garbage in kitchen units and flushing it down the sewer increases the load on sewage-disposal plants and the amount of sewage sludge.

Other alternatives to incineration are abandonment or onsite-burial, transport and disposal in remote areas, and utilization of waste materials.

Since abandoned or buried vegetation can have undesirable or harmful effects (e.g., hosting insects or organisms, producing odors, polluting water, or creating fire hazards), the U.S. Department of Agriculture and State and local agricultural agencies should be consulted about these techniques. Transport and disposal to areas where harmful effects are avoided is not commonly practiced. Large forest scraps processed by chipping or crushing may be utilized as raw materials for kraft pulp mills or processes producing fiberboard, charcoal briquettes, or synthetic firewood;[30] composting or animal-feeding are other possible uses.

High-temperature incineration in excess air is the next most likely means for reducing CO emissions. More than 1 140 K, more than 150 percent excess air, and less than 5.3 kJ/s of heat release for each cubic foot of combustion space are sometimes used as design parameters for incinerators. With these conditions, CO emission rates are less than 0.5 kg/1 000 kg incinerated.[31] (Estimated emission factors for types of incinerators are given in Chapter 5.) Although insufficient air, combustion space, and mixing will increase CO emission rates, the most common cause is low incineration temperature.

Auxiliary burners increase incineration temperature from 1 140 to 1 250 K. Above 1 250 K, slagging of refractories is often a problem. Even for dry combustible wastes that burn above 1 140 K, auxiliary burners are used to preheat the secondary combustion sections of the incinerator before the waste is ignited. On-off temperature controls for small units and modulating controls for large incinerators promote consistent emission reduction.

Air may be supplied by natural or mechanical draft. Stack or chimney dimensions, barometric damper dimensions, and induced-draft fan capacities

for various incinerators, air flows, and wastes are recommended by the Incinerator Institute of America.[32] For the most effective control, air is passed through the grates (underfire air), admitted over the burning waste (overfire air), and admitted into chambers where auxiliary burners are located (secondary air); the ratio of these air supplies varies depending on the incinerator design. For small incinerators, combustion air is regulated by manual adjustment of air ports at the various points of entry; for large incinerators, admission of air and, at times, the ratio between air supply at various points is automatically controlled. For 150 percent excess air, the oxygen content of the undiluted gases at the incinerator outlet ranges between 12 and 14 percent, depending on the type of waste and the type of auxiliary fuel.

Sufficient residence time for oxidation of combustibles is provided by insulating the combustion space. A maximum heat-release of 5.3 kJ/s for each cubic foot is sometimes used for determining required combustion space. Contact between gaseous combustibles and air is promoted by providing baffles, bridge walls, checkerwork, curtain walls, down passes, drop arches, mixing chambers, by introducing air at strategic locations, and by locating auxiliary burners to promote mixing.

4.10.2 Preventing or Extinguishing Fires

From forest wildfires, about 4.26 Gkg of CO are emitted annually.[33] These fires are often caused by lightning or by carelessness. Considerable activity has been and is being directed toward reducing the frequency of occurrence and the severity of these fires. These activities include publishing and advertising information on fire prevention and control, surveillance of forest areas where fires are likely to occur, and various

fire-fighting and control techniques. Information on prevention and control is available from the U.S. Department of the Interior and from State and local agencies.

Controlled burning of forest debris, crop residues, scrub, brush, weeds, grass, and other vegetation is practiced for one or more of the following purposes: (1) to control vegetation, insects, or organisms harmful to plant life, (2) to reduce the volume of waste, (3) to minimize fire hazards, or (4) to improve land. The CO emissions from this burning are about 9.7 Gkg/yr; collection and burning of these wastes in properly controlled incinerators would reduce emission rates from about 30 to 32.5 kg/1 000 kg to as little as 0.5 kg/1 000 kg.[33]

An estimated 1.1 Gkg of CO is emitted each year by burning 530×10^6 m^3 of coal refuse.[33] Either extinguishing or preventing such fires is used to reduce or eliminate emissions. Cooling and repiling, sealing with impervious material, injecting slurries of noncombustibles, minimizing the quantity of combustibles, and preventing ignition are described and discussed in AP-52, Control Techniques for Sulfur Oxide Air Pollutants.[34]

Structural fires emit an estimated 220 Mkg of CO annually.[33] Fire prevention and fire control techniques are used to minimize these expensive sources. Prevention includes fireproofing construction; proper handling, storage, and packaging of flammable materials; and publishing and advertising information. Control includes the use of sprinklers, foam, and inert gas systems for prompt extinguishing and adequate fire-fighting facilities, personnel, and alarm systems. Information on these and other techniques for fire prevention and control are available from local fire departments, the National Fire Protection Association, the National Safety Council, and from fire insurance companies.

4.10.3 Catalytic Oxidation

Catalytic oxidation can effectively convert carbon monoxide to the harmless carbon dioxide. Copper and an unidentified hexavalent-chrome compound impregnated on a support of high surface area can oxidize CO to CO_2 provided sufficient oxygen is present and the temperature is at least 320 K. The method is suitable for removing CO from nitrogen, ammonia synthesis gas, flue gas, automobile exhaust, home heater exhaust, hydrogen, and other gases.[35] An alternate catalyst for oxidation of carbon monoxide contains manganese oxide and lead oxide. This catalyst can withstand temperatures of 770 K and is suitable for automotive applications.[36] Homogeneous catalytic oxidation of carbon monoxide is also possible at ambient temperatures with an aqueous solution containing palladium (II)/ copper (II).[37]

4.11 REFERENCES

1. "Compilation of Air Pollutant Emission Factors." U.S. Dept. of Health, Education, and Welfare, Office of Air Programs, Research Triangle Park, N.C., AP-52, 1972.

2. Statistical Abstract of the United States: 1970. 91st Edition, U.S. Bureau of the Census, Washington, D.C., 1970.

3. Jahrbuch f. Bergbau Energie Mineralöl und Chemie 1971.

4. W. Brocke, Essen, Vortrag v. 21.11.71.

5. Smith, W. A. and C. W. Gruber. "Atmospheric Emissions from Coal Combustion--An Inventory Guide." U.S. DHEW, PHS, National Air Pollution Control Administration. Cincinnati, Ohio. Publication Number 999-AP-24, April 1966, 112 p.

6. "The Cupola and Its Operation." 3d. ed. Des Plaines, American Foundrymen's Society, 1965, 322 p.

7. Danielson, J. A. (ed). "Air Pollution Engineering Manual." USDHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio. PHS Publ. No. 999-AP-40, 1967, 892 p.

8. "Foundry Air Pollution Control Manual." 2d ed. Des Plaines, American Foundrymen's Society, 1967, 66 p.

9. Sugishma, Wasaburo and Sumio Okuda. "Plastic Waste Treatment and Incineration." Kankyo Sozo (Environ. Creation) 1(4):57-61, Nov. 1971.

10. Alexander, W. H. and R. L. Bradley. "Can You Justify a CO Boiler?" Petrol. Refiner. 37:107-112, August 1958.

11. Danielson, J. A. (ed). "Air Pollution Engineering Manual." USDHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio. PHS Publ. No. 999-AP-40, 1967, 892 p.

12. "Fire Protection Manual for Hydrocarbon Processing Plants." Houston, Gulf Publishing Co., Houston, Texas.

13. "Fire Protection Handbook." Boston, National Fire Protection Association, Boston, Mass.

14. Avery, R. E. and H. L. Valentine. "High-Temperature Piping Systems for Petrochemical Processing." In: CEP Technical Manual, Vol. 10, Safety in Air and Ammonia Plants. New York, American Institute of Chemical Engineers, 1968, p. 20-24.

15. Kratosios, G., and W. P. Long. "Experiences with Primary Reformer Furnaces and Transfer Lines." In: CEP Technical Manual, Vol. 10, Safety in Air and Ammonia Plants. New York, American Institute of Chemical Engineers, 1968, p. 8-15.

16. Wright, L. E. "Piping Codes and Standards." Chem. Eng., 75(13): 247-250, June 17, 1968.

17. American Standards Association. Sectional Committee on Code for Pressure Piping, B31. New York, American Society of Mechanical Engineers.

18. James, G. R. "A Look at High Temperature Reformer Piping." In: CEP Technical Manual, Vol. 10, Safety in Air and Ammonia Plants. New York, American Institute of Chemical Engineers, 1968, p. 1-7.

19. Wheeler, D. H. "Fume Control in L-D Plants." J. Air Pollution Contr. Assoc., 18:98-101, February 1968.

20. Schieman, A. D. "Horizontal Vapor-Liquid Separators." Hydrocarbon Process and Petrol. Refiner., 43:155-160, May 1964.

21. Kent, G. R. "Find Radiation Effect of Flares. Hydrocarbon Processing. 47:119-130, June 1968.

22. Soen. H. T. "Flare System Design Simplified." Hydrocarbon Processing, 46:172-176, January 1967.

23. Reed, R. D. "Design and Operation of Flare Systems." Chem. Eng. Progr., 64:53-57, June 1968.

24. Drogin, I. "Carbon Black." J. Air Pollution Control Assoc., 18(4): 216-228, April 1968.

25. Hardison, L. C. "Disposal of Gaseous Wastes." UOP Air Correction Division, Greenwich, Conn. Presented at Seminar on Waste Disposal sponsored by East Ohio Gas Company, Cleveland, May 18, 1967.

26. Cross, Frank L., Jr. "Air Pollution Control." Preprint, Dept. of Commerce, Washington, D. C., and Water Pollution Control Federation, Washington, D. C., 1971. (Presented at the Technical Conference on New Technology in the Solution of Practical Problems in Air and Water Pollution Control, Tokyo, Dec. 7, 1971.)

27. Kirsh, J. B. "Sanitary Landfill." In: Element of Solid Waste Management Training Course Manual, Public Health Service, Cincinnati, Ohio, 1968, p. 1-4.

28. "Air Pollution Problems from Refuse Disposal Operations in the Delaware Valley." Dept. of Public Health, Air Management Services, Philadelphia, Pa., February 1969.

29. Wiley, J. S., et al. "Composting Developments in the U.S." Combust. Sci., 6:2, 5-9, Summer 1965.

30. Private communication with E. K. Taylor. Southwest Air Pollution Control Authority, State of Washington, October 1969.

31. Stenburg, R. L. et al. "Effects of High Volatile Fuel on Incinerator Effluents." J. Air Pollution Control Assoc., 8:376-384, August 1961.

32. IIA Incinerator Standards. New York, Incinerator Institute of America, November 1968.

33. National Air Pollution Control Administration. Reference Book of Nationwide Emissions. U.S. DHEW, PHS, CPEHS, NAPCA, Durham, N.C.

24. Control Techniques for Sulfur Oxide Air Pollutants. US DHEW, PHS, CPEHS, National Air Pollution Control Administration. Washington, D. C., AP-52, January 1969, p. 87-91.

35. Lutchko, John R. and George R. Stoneburner. "Method of Removing Carbon Monoxide from Gases." Calgon Corp., Pittsburgh, Pa., U.S. Patent 3,545,915, Dec. 8, 1970.

36. Kobayashi, Shigehiko, Kazuhide Miyazaki, and Michiaki Yamamoto. "Method and Catalyst for the Purification of Waste Gases Containing Carbon Monoxide." Mitsui Mining and Smelting Co., Ltd., Tokyo, W. Ger. Patent 2,034,053, July 15, 1971.

37. Lloyd, William G. and Donald R. Rowe. "Homogeneous Catalytic Oxidation of Carbon Monoxide." Environ. Sci. Technol., 5(11): 1133-1134, Nov. 1971.

5. EMISSION FACTORS FOR CARBON MONOXIDE SOURCES

An emission factor is a statistical average of the rate at which pollutants are emitted from the burning (or processing) of a given quantity of material. (The factors can be based on some other meaningful parameter, such as the number of miles traveled in a vehicle.) To determine each factor, reliable data from a source or group of sources are gathered, correlated with information on process use, and tabulated. Either an average or a range of values is selected.

Some emission factors are based on limited data; others, on extensive data that are highly variable; and still others, on extensive, consistent data. It is, therefore, important that the precision of the data be evaluated before the factor is used for estimating emissions.

In general, the emission factors for carbon monoxide air pollutants are not precise indicators for any single process even though the details of that process are known. They are more valid when applied to a number of processes.

Emission factors listed in Table 5-1 are for uncontrolled sources, except as noted in the table.

Table 5-1. - UNCONTROLLED EMISSION RATES FOR CARBON MONOXIDE SOURCES[1]

Type of Emission Source		Emission Rate (g/kg)[1]
Stationary Fuel Combustion Sources		
Bituminous Coal:		
Furnaces greater than 30 MJ/S × 10^6--general		0.5
--wet bottom		0.5
--dry bottom		0.5
--cyclone		0.5
Furnaces from (3 to 30 MJ/S)		1.0
Furnaces less than (3 MJ/S)		5.0
Hand-fired units		45.0
Anthracite Coal:		
Dry bottom		0.5
Overfeed stokers--less than (3 MJ/S)		5.0
--greater than (3 MJ/S)		1.0
Hand-fired units		45.0
Fuel Oil:		
Power plant	g/m^3 4.8	
Industrial and commercial--residual	g/m^3 24.0	
--distillate	g/m^3 24.0	
Domestic	g/m^3 599	
Natural Gas:		
Power plant	kg/hm^3 6.4	
Industrial process boilers	kg/hm^3 6.4	
Domestic and commercial heating units	kg/hm^3 320	
Liquified Petroleum Gas (LPG):		
Industrial process furnaces--butane	g/m^3 1.2	
--propane	g/m^3 1.2	
Domestic and commercial furnaces--butane	g/m^3 240	
--propane	g/m^3 228	
Wood and Bark		1.0
		0 to 116
Solid Waste Disposal		
Refuse Incinerators:		
Municipal--multiple chamber, uncontrolled		0 to 116
--with settling chamber and water spray system		0 to 116
Industrial/commercial--multiple chamber		0.5 to 12.5
--single chamber		2.0 to 100
--controlled air		Neg

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR CARBON MONOXIDE SOURCES--Continued

Type of Emission Source			Emission Rate (g/kg)[1]
Flue-fed			10.0
Modified flue-fed			5.0
Domestic single chamber--without primary burner			150
--with primary burner			Neg
Pathological			Neg
Auto Body Incinerators:			
Uncontrolled	kg/car	1.13	
With afterburner	kg/car	Neg	
Conical Burners:			
Municipal refuse			30.0
Wood			65.0
Open Burning:			
Municipal refuse			42.5
Automobile components			62.5
Horticultural refuse--agricultural field burning			50.0
--landscape refuse and pruning			30.0
Wood			25.0
Mobile Combustion Sources			
Gasoline-Powered Motor Vehicles--1970	kg/m^3	324	
--1971	kg/m^3	318	
--1972	kg/m^3	288	
--1973	kg/m^3	270	
--1974	kg/m^3	252	
--1975	kg/m^3	204	
Diesel:			
Trucks and buses	kg/m^3	27.0	
Locomotives	kg/m^3	8.4	
Aircraft:			
Turbofan--jumbo jet	kg/engine-LTO	12.7	
--long range	kg/engine-LTO	11.8	
--medium range	kg/engine-LTO	7.3	
Turbojet	kg/engine-LTO	10.9	
Turboprop	kg/engine-LTO	.91	
Turboshaft	kg/engine-LTO	2.7	
Piston--transport	kg/engine-LTO	137	
--light	kg/engine-LTO	5.4	

See footnote at the end of the table.

UNCONTROLLED EMISSION RATE FOR CARBON MONOXIDE SOURCES--CONTINUED

Type of Emission Source	Emission Rate (g/kg)[1]
Vessels:	
Steamships--underway . . . . . g/km 0.49	
--in-berth . . . . . g/day 36.24	
Motor ships--underway . . . . . g/km 294	
--in-berth . . . . . kg/day 20.9	
Chemical Process Industires	
Ammonia Manufacture:	
Plants with methanator--purge gas	Neg
--storage and loading	--
Plants with CO absorber and regeneration system	
--regenerator exit	100
--purge gas	Neg
--storage and loading	--
Carbon Black Manufacture:	
Channel process	16750
Thermal process	Neg
Furnace--gas	2650
--oil	2250
Charcoal Manufacture:	
With chemical recovery plant	160
Without chemical recovery plant	160
Food and Agricultural Industry	
Meat Smoking:	
Uncontrolled	0.3
Controlled	Neg
Sugar Cane Processing:	
Field burning . . . . . g/m^2 168	
Bagasse burning	--
Metallurgical Industry	
Coke Manufacture:	
Byproduct cooking--charging	0.3
--coking cycle	0.3
--discharging	0.035
Beehive ovens	0.5
Iron Production:	
Blast furnace ore charge	700 to 1050
Sintering discharge	22

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR CARBON MONOXIDE SOURCES--Continued

Type of Emission Source	Emission Rate (g/kg)[1]
Steel Production:	
Basic oxygen furnace	60 to 75
Electric-arc furnace--oxygen lance	9
--no oxygen lance	9
Gray Iron Foundries-cupola furnace	72.5
Mineral Products Industry	
Asphalt Roofing Manufacture:	
Asphalt blowing	0.45
Petroleum Industry	
Petroleum Refineries:	
Boilers and process heaters--oil burned	Neg
--gas burned	Neg
Fluid catalytic cracking units (FCC) kg/m^3 fresh feed	39.1
Moving-bed catalytic cracking units (TCC) kg/m^3 fresh feed	11.5
Compressor internal combustion engines--kg/10^3 m^3 gas burned	Neg
Wood Processing	
Sulfate Pulping:	
Recovery boilers and direct-contact evaporators	
--untreated	30.0
--venturi scrubber	30.0
--electrostatic precipitators	30.0
Lime kilns--untreated	5.0
--scrubber	5.0

[1]Units other than g/kg are given at the end of the entries immediately preceding numerical values for uncontrolled rates; when controlled rates are known, they are listed by type of control applied.

5.1 REFERENCE

1. Compilation of Air Pollutants Emission Factors. U.S. Dept. of Health, Education, and Welfare, Office of Air Programs, Research Triangle Park, N.C., AP-52, 1972.

U.S. GOVERNMENT PRINTING OFFICE:1973 546-311/93 1-3